LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

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LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

ABSTRACT

The Energy & Environmental Research Center (EERC) is conducting a consortium-based effort directed toward resolving the mercury control issues facing the lignite industry. Specifically, the EERC team—the EERC, the Electric Power Research Institute (EPRI), URS Corporation (URS), ADA-ES, Inc., the Babcock & Wilcox Company, the North Dakota Industrial Commission, SaskPower, and the Mercury Task Force, which includes Basin Electric Power Cooperative, Otter Tail Power Company, Great River Energy, TXU Energy (TXU), Montana—Dakota Utilities Co., Minnkota Power Cooperative, Inc., BNI Coal, Ltd., Dakota Westmoreland Corporation, and North American Coal Corporation—has undertaken a project to significantly and cost-effectively oxidize elemental mercury (Hg⁰) in lignite combustion gases, followed by capture in a wet scrubber. The applicability of this approach is expected to increase because of an expected demand for scrubbed systems in lignite utilities as well as subbituminous utilities in the United States and Canada. The oxidation process is proven at the pilot scale and in short-term full-scale tests. Additional optimization is continuing on oxidation technologies, and this project focuses on monthlong full-scale testing.

The lignite industry has been proactive in advancing the understanding of, and identifying control options for, Hg in lignite combustion flue gases. Approximately 3 years ago, the EERC and EPRI began a series of Hg-related discussions with the Mercury Task Force as well as utilities firing Texas and Saskatchewan lignites. This project is one of three being undertaken by the consortium to perform large-scale Hg control technology testing to address the specific needs and challenges to be met in controlling Hg from lignite-fired power plants.

This project involves Hg oxidation upstream of a system equipped with an electrostatic precipitator (ESP) followed by wet flue gas desulfurization (FGD). The project team involved in conducting the technical aspects of the project includes the EERC, Babcock & Wilcox, EPRI, URS, and ADA-ES. The host sites include Minnkota Power Cooperative Milton R. Young (MRY) Station Unit 2 and TXU Monticello Steam Electric Station (MoSES) Unit 3. The work involves establishing Hg oxidation levels upstream of air pollution control devices (APCDs) and removal rates across existing ESP and FGD units, determining costs associated with those removal rates, investigating the possibility of the APCD acting as a multipollutant control device, quantifying the balance-of-plant impacts of the control technologies, and facilitating technology commercialization.

MRY Station

The full-scale field testing at MRY included 2 weeks of parametric testing after which 6 weeks of long-term testing evaluated the performance of one mercury oxidation agent. The preliminary results indicated that higher-than-expected rates of SEA2 were required in order to obtain mercury removal rates above 75%. The longer-term test of SEA2 along with a small

amount of powdered activated carbon (PAC) was conducted, resulting in at least 50% mercury removal rates during 75% of the test.

Monticello Station

Full-scale boiler halogen injection tests were performed at MoSES Unit 3 to evaluate mercury oxidation and removal across a cold-side ESP/wet FGD system. Short-term parametric tests were followed by two 2-week continuous Br injection tests. Preliminary analysis of the data indicates that the mercury removal rate across the APCD ranged from 44% to 89% during long-term tests depending on the Br injection rate.

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NOMENCLATURE

AHI air heater inlet AHO air heater outlet

APCD air pollution control device B&W Babcock & Wilcox Company

BOP balance of plant

CMM continuous mercury monitor DOE U.S. Department of Energy

ECM economizer

EERC Energy & Environmental Research Center
EPA U.S. Environmental Protection Agency
EPRI Electric Power Research Institute

ESP electrostatic precipitator

FF fabric filter

FGD flue gas desulfurization
Hg⁰ elemental mercury
Hg²⁺ mercuric compounds
HgCl₂ mercuric chloride

ICR Information Collection Request (EPA)

IGS inertial gas separationMRY Milton R. Young Station

NDIC North Dakota Industrial Commission NETL National Energy Technology Laboratory

OH Ontario Hydro

PAC powdered activated carbon

pc pulverized coal QA quality assurance QC quality control

SCA specific collection area

SCEM semicontinuous emission monitor

SDA spray dryer absorber

SEA sorbent enhancement additive SEM scanning electron microscopy

SOA solid oxidizing additive

TXU TXU Energy
URS URS Corporation

LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

EXECUTIVE SUMMARY

The Energy & Environmental Research Center (EERC) is conducting a consortium-based effort directed toward resolving the mercury control issues facing the lignite industry. Specifically, the EERC team—the EERC, the Electric Power Research Institute (EPRI), URS Corporation (URS), ADA-ES, Inc., the Babcock & Wilcox Company, the North Dakota Industrial Commission, SaskPower, and the Mercury Task Force, which includes Basin Electric Power Cooperative, Otter Tail Power Company, Great River Energy, TXU Energy (TXU), Montana—Dakota Utilities Co., Minnkota Power Cooperative, Inc., BNI Coal, Ltd., Dakota Westmoreland Corporation, and North American Coal Corporation—has undertaken a project to significantly and cost-effectively oxidize elemental mercury (Hg⁰) in lignite combustion gases, followed by capture in a wet scrubber. The applicability of this approach is expected to increase because of an expected demand for scrubbed systems in lignite utilities as well as subbituminous utilities in the United States and Canada. The oxidation process is proven at the pilot scale and in short-term full-scale tests. Additional optimization is continuing on oxidation technologies, and this project focuses on monthlong full-scale testing.

The lignite industry has been proactive in advancing the understanding of, and identifying control options for, Hg in lignite combustion flue gases. Approximately 3 years ago, the EERC and EPRI began a series of Hg-related discussions with the Mercury Task Force as well as utilities firing Texas and Saskatchewan lignites. This project is one of three being undertaken by the consortium to perform large-scale Hg control technology testing to address the specific needs and challenges to be met in controlling Hg from lignite-fired power plants.

This project involves Hg oxidation upstream of a system equipped with an electrostatic precipitator (ESP) followed by wet flue gas desulfurization (FGD). The project team involved in conducting the technical aspects of the project includes the EERC, Babcock & Wilcox, EPRI, URS, and ADA-ES. The host sites include Minnkota Power Cooperative Milton R. Young (MRY) Station Unit 2 and TXU Monticello Steam Electric Station (MoSES) Unit 3. The work involves establishing Hg oxidation levels upstream of air pollution control devices (APCDs) and removal rates across existing ESP and FGD units, determining costs associated with those removal rates, investigating the possibility of the APCD acting as a multipollutant control device, quantifying the balance-of-plant impacts of the control technologies, and facilitating technology commercialization.

MRY Station

The full-scale field testing at MRY was carried out during March, April, and May 2005. The test plan included 2 weeks of parametric testing after which 6 weeks of long-term testing evaluated the performance of one mercury oxidation agent. Parametric testing included three mercury oxidation enhancement agents (SEA1, SEA2, and MgCl₂) at several rates alone and with carbon-based sorbent injection. SEA2 was determined to be the most effective agent. The

longer-term field testing (6 weeks) of chemical addition was conducted to enhance Hg oxidation and capture in the ESP and wet FGD at the MRY plant. The preliminary results indicated that higher-than-expected rates of SEA2 were required in order to obtain mercury removal rates above 75%. The longer-term test of SEA2 along with a small amount of powdered activated carbon (PAC) was conducted, resulting in at least 50% mercury removal rates during 75% of the test.

The baseline corrosion probes were characterized to determine whether the test methods yielded any increased corrosion. Preliminary results indicate a change in the texture of the probe surface during the long-term test. Chemical analysis of the coals fired during the testing periods will be used to determine whether the change is related to the fuels or to the oxidizing agents.

Monticello Station

Full-scale boiler halogen injection tests were performed at MoSES Unit 3 to evaluate mercury oxidation and removal across a cold-side ESP/wet FGD system. Short-term parametric tests were followed by two 2-week continuous injection tests. Parametric tests occurred on October 27–30, 2005, and evaluated two mercury oxidation agents: CaCl₂ and CaBr₂. The CaCl₂ was injected at rates ranging from 400 to 800 ppm of the active reagent (AR) in the coal. The CaBr₂ was injected at rates ranging from 12 to 200 ppm AR in the coal. Based on the results, CaBr₂ was selected for the long-term tests.

The long-term tests were executed as two 2-week periods of CaBr₂ injection. Baseline measurements were made prior to the start of each long-term period. In the first 2-week period (November 5–18, 2005), the target injection rate was 50 ppm Br in the coal; for the second 2-week period (December 2–14, 2005), the primary target injection rate was 100 ppm Br in the coal. During each long-term test, flue gas mercury concentrations were monitored continuously at the ESP inlet, ESP outlet, and FGD outlet. Daily process samples of coal, fly ash, and FGD were gathered. Preliminary analysis of the data indicates that the mercury removal rate across the APCD ranged from 44% to 89% during long-term tests depending on the Br injection rate.

LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

1.0 INTRODUCTION

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The lignite industry has been proactive in advancing the understanding of and identifying control options for Hg in lignite combustion flue gases. Approximately 3 years ago, the EERC and EPRI began a series of Hg-related discussions with the Mercury Task Force as well as utilities firing Texas and Saskatchewan lignites. This project is one of three being undertaken by the consortium to perform large-scale Hg control technology testing to address the specific needs and challenges to be met in controlling Hg from lignite-fired power plants.

This project involves Hg oxidation upstream of a system equipped with an electrostatic precipitator (ESP) followed by wet flue gas desulfurization (FGD). The project team involved in conducting the technical aspects of the project includes the EERC, B&W, EPRI, URS, and ADA-ES. The host sites include Minnkota Power Cooperative Milton R. Young (MRY) Unit 2 near Center, North Dakota, and TXU Monticello Steam Electric Unit 3 near Mt. Pleasant, Texas. The work will involve establishing Hg oxidation levels upstream of air pollution control devices (APCDs) and removal rates across existing ESP and FGD units, determining costs associated with those removal rates, investigating the possibility of the APCD acting as a multipollutant control device, quantifying the balance-of-plant (BOP) impacts of the control technologies, and facilitating technology commercialization.

The other projects cover sorbent injection technologies for systems equipped with ESPs and those equipped with spray dryer absorbers combined with fabric filters (SDA–FF) and an alternative oxidation technology. The intent of the proposed testing is to help maintain the viability of lignite-fired energy production by providing utilities with lower-cost options for meeting future Hg regulations.

2.0 BACKGROUND

Mercury is an immediate concern for the U.S. electric power industry because of the U.S. Environmental Protection Agency (EPA) December 2000 decision that regulation of Hg from coal-fired electric utility plants is appropriate and necessary under Section 112 of the Clean Air Act (1). EPA determined that Hg emissions from power plants pose significant hazards to public health and must be reduced. The EPA *Mercury Study Report to Congress* (2) and the *Utility Hazardous Air Pollutant Report to Congress* (3) identified coal-fired boilers as the largest single source of atmospheric Hg emissions in the United States, accounting for about one-third of the total anthropogenic emissions. On December 15, 2003, EPA published the proposed Utility Mercury Reductions Rule in order to solicit comments on multiple approaches for mercury emission control. EPA reviewed comments on the proposed rule and put forth regulations in March 2005.

Even though Hg regulations for coal-fired utilities are imminent, significant issues remain and need to be resolved. The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) has acknowledged that data gaps exist for Hg control technologies for the immense U.S. reserves of lignite and subbituminous coals. The primary challenge is that these coals produce flue gases in which difficult-to-control Hg⁰ is the dominant form. The EPA Information Collection Request (ICR) indicates that questions still exist regarding the impact of various APCDs and technologies for lignite-fired units on their ability to control Hg⁰ emissions. The lignite-based consortium believes that there is a critical need for large-scale Hg oxidation testing at lignite-fired power plants equipped with an ESP and wet FGD. This project has been developed based on the input of consortium members and DOE guidance to address these issues.

In general, lignitic coals are unique because of their highly variable ash content, which is rich in alkali and alkaline-earth elements and has high oxygen and moisture levels and low chlorine content. Lignite coals typically contain comparable levels of Hg but significantly lower levels of chlorine compared to bituminous coals. Lignites have chlorine concentrations well below 200 ppm in the coal, whereas Appalachian and Illinois Basin bituminous coals can have chlorine levels in excess of 1000 ppm. These differences in composition have important effects on the form of Hg emitted from a boiler and the capabilities of different control technologies to remove Hg from flue gas. Coals containing chlorine levels greater than 200 ppm typically produce flue gas dominated by more easily removable mercuric compounds (Hg²⁺), most likely mercuric chloride (HgCl₂). Conversely, experimental results indicate that low-chlorine (<50 ppm) coal combustion flue gases (typical of lignite) contain predominantly Hg⁰, which is substantially more difficult to remove than $\mathrm{Hg}^{2+}(3)$. Additionally, the generally high alkali and alkaline-earth content of lignite coals may reduce the oxidizing effect of the already-low chlorine content by reactively scavenging chlorine species (Cl, HCl, and Cl₂) from the combustion flue gas. The level of chlorine in flue gases of recently tested lignites from North Dakota and Saskatchewan ranged from 2.6 to 3.4 ppmv, with chlorine content ranging from 11 to 18 ppmw in the coal on a dry basis, respectively.

Few published data exist that demonstrate the effectiveness of oxidation technologies for plants firing lignite coal. Lignite-fired power plants have shown a limited ability to control Hg emissions in currently installed ESPs, SDAs, and wet FGD systems (4). This low level of control

can be attributed to the high proportions of Hg^0 present in the flue gas. Typically, in the pulverized coal (pc)- and cyclone-fired units, the Hg^0 content is greater than 85% of the total; the average emitted from North Dakota lignite-fired power plants is roughly 6.3 lb/TBtu (4, 5). Figure 1 shows resulting Hg emissions measured using the Ontario Hydro (OH) method and continuous mercury monitors (CMMs) at the furnace exit during pilot tests at the EERC with North Dakota lignite. These results are consistent with the ICR results discussed above and with the recent baseline data for the proposed test sites, as shown later.

The mercury oxidation technologies being investigated for lignites include catalysts and chemical agents. The catalysts that have been tested include selective catalytic reduction catalysts for NO_x reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts (chloride compounds) and cofiring fuels that contain oxidizing agents (6, 7).

Theoretically, the use of chloride compounds to oxidize Hg⁰ to Hg²⁺ makes sense. The evidence includes chemical kinetic modeling of bench-scale test results, indicating that the introduction of chloride compounds into the high-temperature furnace region will likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg⁰ reactants in coal combustion flue gases (6). The formation of atomic chlorine is a key pathway involved in the chemical reaction mechanisms that result in the oxidation of Hg⁰ (6). The pathway for Hg oxidation is gas-phase Hg⁰ oxidation by atomic chlorine (chlorine radical). Recent kinetic modeling of chlorine radical formation as a function of temperature

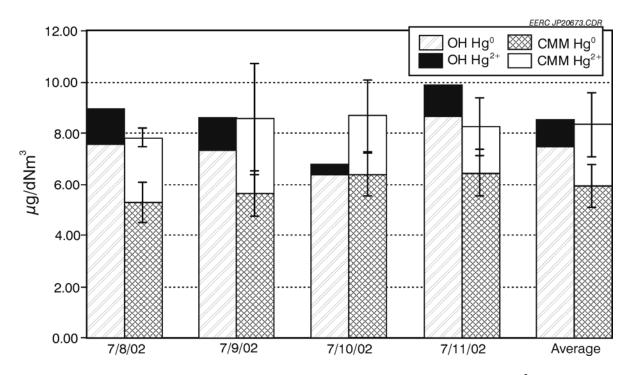


Figure 1. Inlet mercury speciation for Freedom, North Dakota, lignite ($\mu g/dNm^3 = microgram$ per dry normal cubic meter [corrected to 0°C and 3% O₂]).

and residence time is shown in Figure 2. The results indicate the importance of temperature in the abundance of chlorine radicals. Recent work, supported by EPRI, indicated that the injection of HCl in lower-temperature regions downstream of the boiler was ineffective in oxidizing Hg⁰, while the injection of salt into the furnace resulted in significant oxidation (8).

Fuel additives for Hg oxidation have recently been tested in a pilot-scale system. Chemical additives or oxidants such as chloride salts have shown the ability to convert Hg⁰ to more reactive oxidized forms, as shown in Figure 3. In addition, recent EPRI short-term testing conducted at a 70-MW_e pc-fired North Dakota power plant indicated that the injection of chloride salts can result in increased Hg oxidation in the flue gas (8). Hg oxidation of up to 70% was observed at a salt injection rate that resulted in an HCl concentration of 110 ppm in the flue gas, as shown in Figure 4. In addition, the injection of salt resulted in the enhanced removal of Hg across the SDA–FF, with removal efficiencies of up to 50% in short-term field testing (8).

Because of the promise seen in the oxidation of Hg in flue gases produced from lignite coals, the project team is conducting long-term field testing of Hg oxidation and removal using a wet FGD at MRY Unit 2 and Monticello Unit 3.

MRY Unit 2 is a B&W Carolina-type radiant boiler designed to burn high-moisture, high-slagging/fouling North Dakota lignite. Nominally rated at 3,050,000 lb/hr, this unit is a cyclone-fired, balanced-draft, pump-assisted circulation boiler. The unit began commercial operation in May 1977 and is base-loaded at 450 MW gross. The unit is equipped with a cold-side ESP for particulate control and a wet FGD unit for SO₂ control. The cold-side ESP has a specific

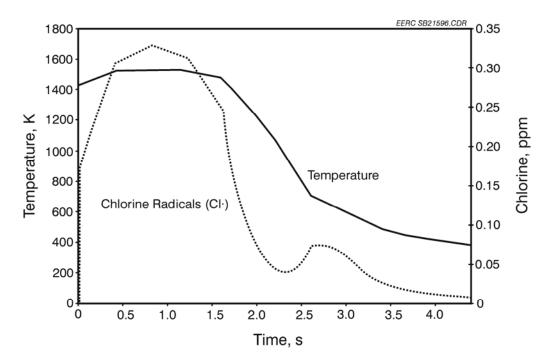


Figure 2. Prediction of chlorine radical formation as a function of temperature and residence time typical of a utility boiler using a kinetic model (Chemkin).

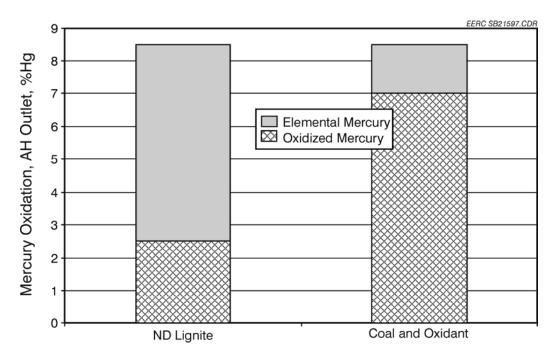


Figure 3. Oxidation of mercury through the addition of a chlorine-containing additive to the coal in EERC pilot-scale testing.

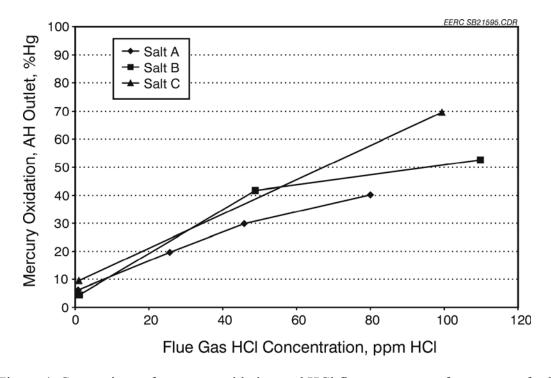


Figure 4. Comparison of mercury oxidation and HCl flue gas content for a range of salt injections at a North Dakota lignite-fired power plant (8).

collection area (SCA) of 375 ft²/1000 acfm. The wet FGD for SO₂ control utilizes alkaline ash and lime. The MRY Plant fires North Dakota lignite coal from the Kinneman Creek and Hagel seams at the Center Mine. This plant and configuration are ideal for testing Hg oxidation and control in a wet scrubber. The high-temperature environment in the cyclone will easily vaporize and transform the chlorine species into highly reactive radical forms. The system has been tested for Hg speciation and control.

Flue gas sampling for speciated Hg was conducted on MRY Unit 2 at the ESP inlet, FGD inlet, and stack from October 22 through November 14, 2002. The sampling was carried out using both the OH method and CMMs (9). A schematic of the plant and sample locations is in Figure 5. The sampling involved the OH method at the ESP inlet, FGD inlet, and stack. In addition to OH method sampling, two CMMs, one at the FGD inlet and one at the stack, were used to monitor speciated Hg levels. The CMMs were operated to obtain 20 days of data at the two locations.

The average Hg speciation results from Unit 2 OH method flue gas sampling are summarized in Figure 6A. The average Hg emissions at the stack were 95% Hg 0 . Two CMMs were operated at the FGD inlet and stack locations of Unit 2 to gather Hg variability data. Statistical analysis of the CMM data indicates that the average Hg concentration was $10.7 \pm 2.7 \, \mu g/m^3$ (90th percentile) at the FGD inlet and $9.3 \pm 2.2 \, \mu g/m^3$ at the stack. Hg-level fluctuations resulting from minor coal changes as well as other variability in plant operations were found to fall within 24% of the average. A Hg balance for MRY Unit 2 (10) was determined by comparing the rate of Hg entering the plant to the rate of Hg leaving the plant. The resulting material balances ranged from 102% to 103%.

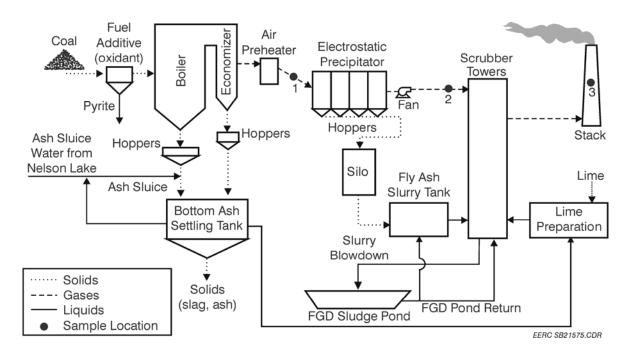


Figure 5. Schematic for MRY Unit 2 showing sampling locations.

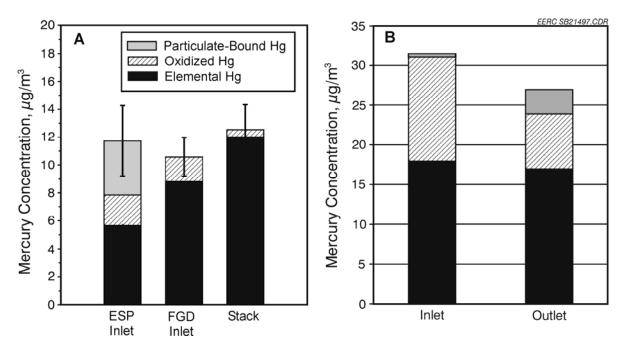


Figure 6. A) MRY OH mercury data obtained in October–November 2002 and B) OH mercury data for Monticello (ICR data).

The second site is TXU Monticello Unit 3 located near Mt. Pleasant, Texas. This site is also well characterized for Hg speciation, emissions, and variability. In addition, it provides an opportunity to test the Hg oxidation technology on a Texas lignite. Figure 7 illustrates the Unit 3 gas path. Unit 3 has a 750-MW B&W wall-fired, Carolina-type universal pressure boiler that fires Texas lignite coal from the upper and lower Wilcox seam. The unit was placed in commercial operation in 1978 and fires 640 tons/hr of Texas lignite at full-rated load. Downstream of the air preheater, the gas flows through a cold-side ESP constructed by Hamon Research-Cottrell, Inc. The ESP has ten fields with a SCA of 900 ft²/1000 acfm. The ESP outlet temperature is nominally 300°F.

The results of Hg speciation measurements at the inlet and outlet of the scrubbers at Monticello Unit 3 are shown in Figure 6B. The results of the OH method sampling indicate that 57% of the total Hg is in the elemental form entering the wet FGD and that the Hg⁰ is not captured with the wet FGD. Results from the ICR tests at Monticello Unit 3 suggest approximately 15% Hg removal across the FGD system, which is consistent with the trends for other units firing low-rank lignite coals.

3.0 EXPERIMENTAL

3.1 Objectives

The objective of this project is to demonstrate the effectiveness of chemical addition for reducing Hg emissions from flue gas derived from lignite. Full-scale tests will be performed at

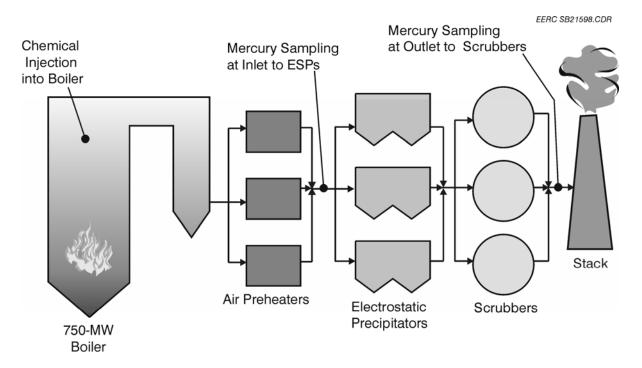


Figure 7. Plant schematic for Monticello Unit 3.

MRY Unit 2 and Monticello Unit 3 to evaluate chemical addition performance across an ESP wet scrubber configuration.

The objective of MRY Unit 2 testing is to determine the impact of chemical addition on Hg speciation, overall Hg removal from the flue gas using the combination of the ESP and wet scrubber, and the impact of the additive salts on corrosion and deposition on system components. The objective of Monticello Unit 3 testing is to provide additional data on Hg oxidation and removal efficiency when a lignite coal from Texas is fired. Data from this program will be used to perform an economic analysis of the costs associated with full-scale implementation of a chemical addition system.

3.2 Planned Scope of Work

The scope of work includes testing oxidation technology for controlling Hg emissions at two lignite-fired power plants equipped with wet FGD systems. The plants include MRY Unit 2 (cyclone-fired, North Dakota lignite, ESP, wet FGD) and Monticello Unit 3 (wall-fired, Texas lignite, ESP, wet FGD). The technology involves the injection of a chemical additive (sorbent enhancement additive [SEA]) with the lignite or injection into the furnace to oxidize Hg upstream of a wet FGD system. The two plants with different firing systems and lignite types will be tested to determine the following: the degree of mercury oxidation as a function of chemical addition rate, Hg removal efficiencies, economics, and BOP impacts. The additive will be added at rates equivalent to 300–1000 ppm chlorine in the coal during parametric testing, with a target of less than 500 ppm in the coal for the long term if selected. A second additive (SEA2) has repeatedly been shown to be even more effective than chlorine and will therefore be tested,

as well. In addition, small amounts of solid oxidizing additive (SOA [activated carbon in this case]) will be added (<1 lb/Macf) to further enhance oxidation. The 2-month test will be conducted using the additive that performs the best during parametric testing. If fractions of lb/Macf of carbon are shown effective in enhancing the SEA impact, it will also be considered for the 2-month test.

4.0 RESULTS AND DISCUSSION

4.1 Summary of Activities Conducted April – June 2005

4.1.1 MRY Plant

In the previous reporting period, a meeting on-site was conducted with MRY personnel, a detailed test plan was finalized, and corrosion probes were installed at the MRY plant November 18, 2004. During this reporting period, longer-term testing of the oxidizing agent along with a small amount of powdered activated carbon (PAC) was conducted. In addition, the baseline corrosion probes were removed and replaced with probes to be exposed during the 4-week test period. Mercury sampling and measurement were conducted using CMM and OH method sampling.

4.1.2 Monticello Plant

Planning is under way for testing at Monticello, which will follow the MRY tests. A draft of the testing plan was prepared and sent to project sponsors and participants for their review. A meeting between the EERC and URS was conducted to provide URS personnel an overview of the testing results obtained at the MRY plant.

4.2 Results from MRY Testing

The work conducted the January – March 2005 quarter consisted of characterization of the corrosion probes. The results of the probe characterization are discussed in detail in Section 4.2.7. Sections 4.2.1 through 4.2.6 were conducted in prior quarters.

4.2.1 Installation of Oxidant and PAC Injection Systems

The oxidant or SEA injection system consists of liquid storage tanks, a metering and pumping skid, and injection lances. Three tanks for storage and diluting the solutions of SEA are shown in Figure 8. Each tank has a storage capacity of 3100 gallons. The SEA pumping and metering skid is shown in Figure 9. This system is capable of pumping the SEA solutions at rates of 0.1 to 2.2 gal/min. This allowed for the injection of SEA at rates up to 500 ppm on an as-fired coal basis. The SEA was injected into the coal pipes prior to being fed into the cyclones. The injection of SEA was conducted at four cyclones. The injection lances are shown in Figure 10.



Figure 8. Oxidant or SEA storage tanks at MRY.



Figure 9. SEA pumping and metering skid.

In addition to the SEA injection system, a PAC injection system was installed that allowed for the injection of a small amount of PAC upstream of the ESP. The PAC consisted of an Apogee portapac metering skid, blower, connecting lines, and injection lances. The injection of carbon was conducted at 16 locations into the ductwork upstream of the ESP, as shown in Figure 11. In addition, the location upstream of the ESP was also for OH method sampling and CMM. The other locations for mercury sampling and measurement were between the ESP and scrubber, as well as at the stack. The stack location is illustrated in Figure 12.



Figure 10. SEA injection lances shown installed at MRY.



Figure 11. PAC injection and OH and CMM sampling locations.



Figure 12. OH and CMM mercury-sampling and measurement location on the stack.

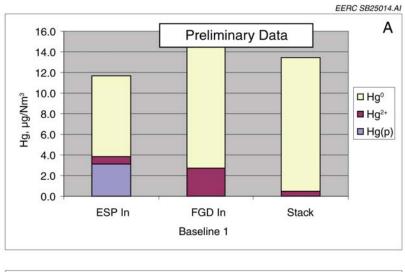
4.2.2 Baseline and Parametric Testing

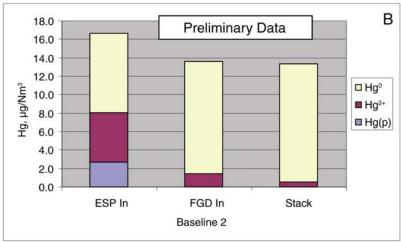
The baseline and parametric testing was initiated with baseline testing on March 15 and completed in early April 2005. During the baseline testing, OH and CMM measurements were made. Following the baseline testing, three rates of PAC were tested to determine the removal with PAC alone. The next testing was conducted with SEA1 (CaCl₂) alone. This testing was followed by combining both SEA1 and PAC at three rates. In addition, a short test was conducted with MgCl₂ to determine the differences between the types of oxidant. SEA2 was injected following the testing of SEA1. SEA2 was injected at three rates and was combined with PAC. All of the data that will be presented are preliminary and have not gone through complete quality assurance/quality control (QA/QC). Not all the coal analyses and other data were available for interpreting the results presented in this report.

Baseline OH method testing is shown in Figure 13 for the three replicate tests. The baseline values at this time are preliminary and have not been compared to coal mercury levels. The results show that the total level of Hg at the inlet varies from about 12 to $16~\mu g/Nm^3$. The speciation at the inlet does not represent forms of Hg in the flue gas stream because of the reaction of the dust cake formed on the filter with the gas-phase mercury. The measurements downstream of the ESP after the particulate materials have been removed are more representative of the mercury species present in the flue gas. The elemental form is the most abundant at the FGD inlet and at the stack. The results indicate very little removal across the ESP/FGD. The results shown in Figure 13A are typical of past testing results, as shown in Figure 6A.

4.2.3 Mercury Speciation with SEA and Carbon Addition

The aim of the project was to add components to the coal to enhance the formation of oxidized and particulate forms of mercury, thus enabling the capture of mercury in the ESP and wet FGD. The first SEA tested was CaCl₂. These injection rates are on a dry-coal basis. The mercury speciation in the flue gas derived from the combustion of Center lignite with the addition of CaCl₂ is shown in Figure 14. The results indicate that the abundance of oxidized and





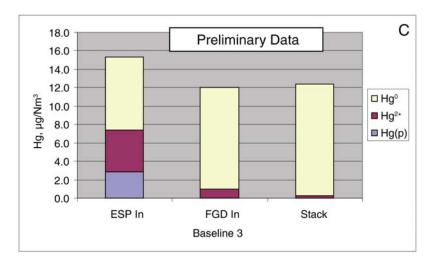
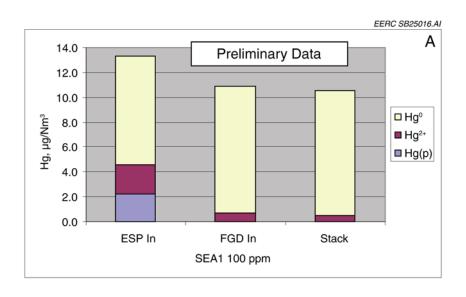
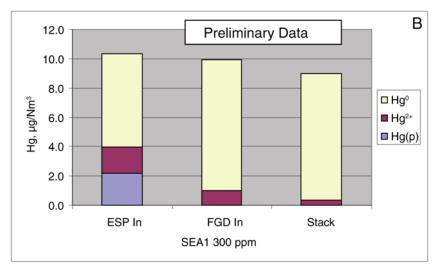


Figure 13. Preliminary baseline OH method measurements at the A) ESP inlet, B) FGD inlet, and C) stack.





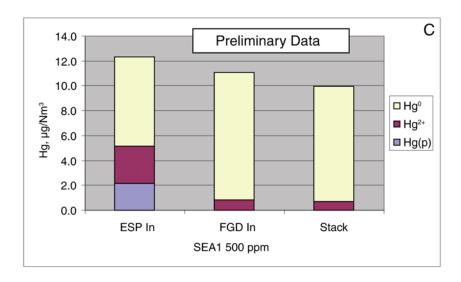


Figure 14. Mercury speciation with SEA1 added to coal.

particulate forms of mercury only increase slightly with the addition of CaCl₂ up to 500 ppm. These results differ significantly from the testing that was conducted in the EERC pilot-scale system where the degree of oxidation increased dramatically with the addition of CaCl₂ (11). The differences may be the result of the cyclone firing and the differences in coal characteristics. The cyclone firing will enhance the presence of alkali and alkaline-earth elements in the fly ash. In addition, the Center lignite fired during the testing has a high level of sodium. Sodium, along with calcium, has the potential to react with the chlorine and likely decrease its potential to react with elemental mercury.

Testing was also conducted using SEA2, which has shown significant promise in oxidizing Hg⁰ and converting it into the particulate and oxidized forms. Figure 15 shows the forms of mercury and the levels of mercury at the ESP inlet, FGD inlet, and stack. The SEA2 significantly increases the level of particulate forms of mercury with only 25 ppm added on an as-fired-coal basis. The particulate and some of the oxidized forms of mercury are removed across the ESP. The remaining Hg⁰ and Hg²⁺ were not removed by the FGD. Most of the removal occurred in the ESP.

4.2.4 Mercury Control with SEA Addition Only

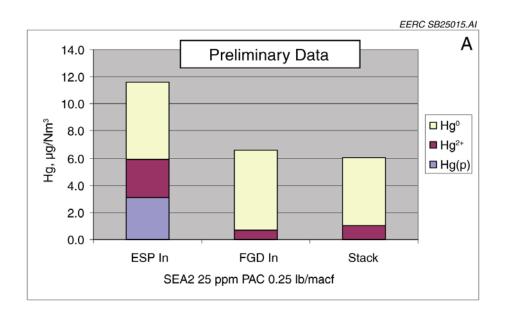
The mercury removal attained with the addition of SEA1, SEA2, and MgCl₂ across both the ESP and FGD is shown in Figure 16. The CaCl₂ and MgCl₂ show similar results. The SEA2 shows appreciably higher removal rates with the addition of much smaller quantities. However, the goal of 55% removal was not achieved using up to 75 ppm addition of SEA₂. Surprisingly, nearly all of the mercury removal occurred in the ESP with little removal occurring in the FGD. It appears that what mercury is oxidized is removed in the ESP, with the remaining mercury in elemental form, which passes through the FGD. The SEA1 was not particularly effective in oxidizing and removing mercury, with stack CMM measurements indicating only 16% removal at 500 ppm SEA1 (ppm halogen on a dry-coal basis). The OH method measurements indicate a similar removal at the same SEA1 concentration based on stack OH method total mercury measurements relative to baseline.

The SEA2 shows appreciably higher removal rates with addition of much smaller quantities. However, the ability to achieve the goal of 55% removal was not achieved using up to 75 ppm addition of SEA2 which resulted in only 44% removal, as shown in Figure 17.

Although achieving higher mercury removal with smaller quantities of material, the behavior of the SEA2 is similar to that of SEA1 in that nearly all mercury removal occurred across the ESP, and the mercury exiting the ESP is primarily in elemental form.

4.2.5 Mercury Control with SEA and Carbon Injection

SEA with the addition of small amounts of carbon has been shown to enhance the oxidation of mercury as well as its capture (11). The results obtained at the MRY Station during parametric testing is shown in Figure 18. The results with PAC only show removals up to 35% with the addition of 1 lb/Macf. The addition of SEA1 showed some improvement at lower PAC



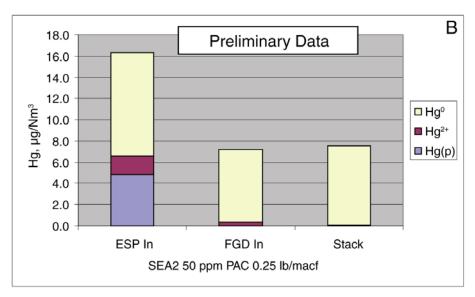


Figure 15. Mercury speciation with SEA2 and PAC addition.

addition rates, but showed no significant improvement at higher PAC addition rates. The improvement in capture using SEA1 with carbon was not as significant as the results obtained in other projects. The reason is likely the high sodium content and the ash partitioning during the cyclone combustion process. The results obtained with the combination of SEA2 and PAC showed much better removal than observed with SEA2 alone.

SEA1 in combination with PAC injection resulted in improved mercury removal as shown in Figure 19. At the highest rates tested of 300 ppm SEA1 with 1.00 lb/Macf PAC, the removal was 35% based on stack CMM measurements. However, this is significantly lower than the goal

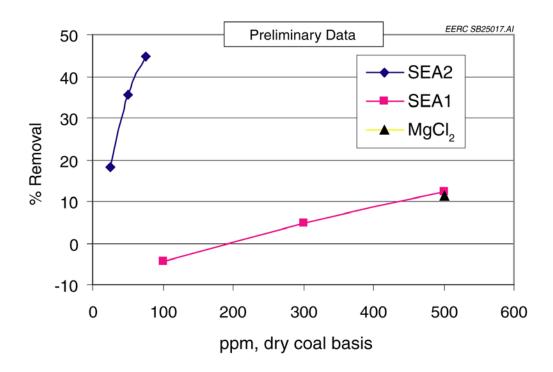
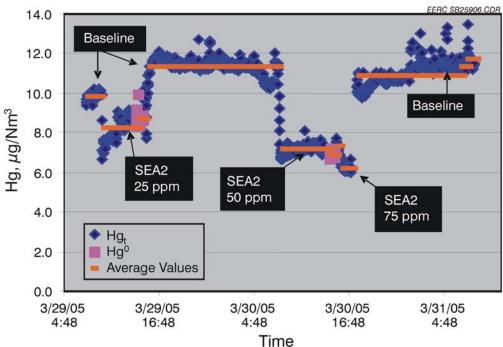


Figure 16. Mercury reduction across ESP and FGD using SEA only.



Time Figure 17. Mercury stack measurements conducted during the injection of SEA2.

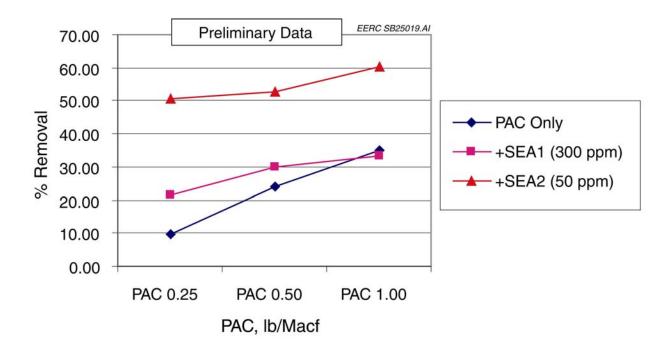


Figure 18. Mercury reduction with SEA or PAC.

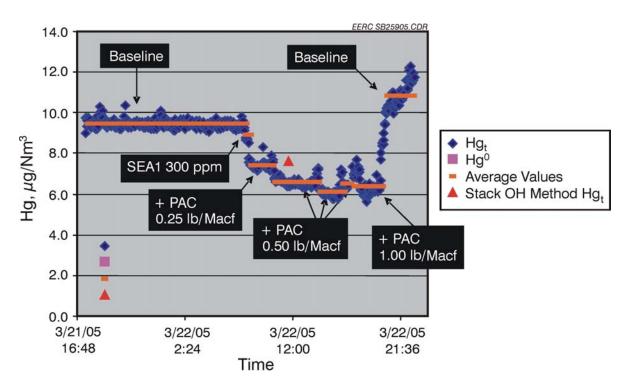


Figure 19. Mercury stack measurements during the injection of SEA1 and PAC.

of 55% removal. Again, nearly all of the mercury removal occurred across the ESP, with primarily Hg⁰ exiting the ESP.

PAC alone performed nearly as well as when injected in combination with SEA1, achieving approximately 35% removal at a rate of 1.00 lb/Macf; at 1.80 lb/Macf, there was 53% mercury removal, which was near the 55% goal. The objectives of the project, however, precluded the use of PAC at such a high rate.

The results obtained at the MRY Station of SEA2 addition in combination with PAC injection are shown in Figure 20. These results, obtained with the combination of SEA2 and PAC, showed much better removal than observed with SEA2 alone. It was possible to obtain removals of 50% or better with 50 ppm SEA2 and 0.3–0.5 lb/Macf PAC.

4.2.6 Extended Testing at MRY

The objective of the extended testing was to demonstrate that approximately 55% mercury removal could be obtained over a period of a month or more. Initially, this was attempted using SEA2 injection alone at injection rates of 60–100 ppm. The mercury removal rates for the extended period are shown in Figure 21. It is noted that removal as high as 75% was achieved during the first portion of the long-term testing, but only at SEA2 injection rates greater than 100 ppm. It was then determined that SEA2 injected at these rates, along with a small quantity (0.15 lb/Macf) of PAC, was required to meet the target of 55% mercury removal. As previously noted, the injection of SEA2 or SEA2 and PAC precludes obtaining a baseline value while the injections are under way. The percentage of mercury removal for the extended testing is based

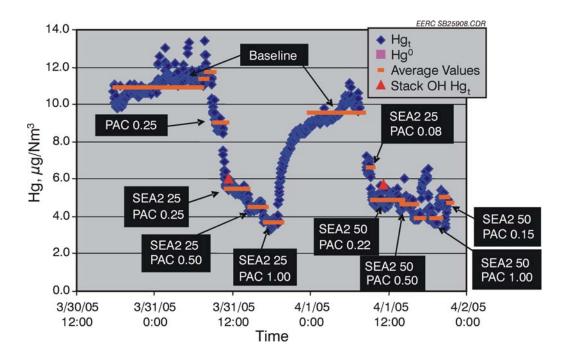


Figure 20. Mercury stack measurements conducted during injection of SEA2 and PAC.

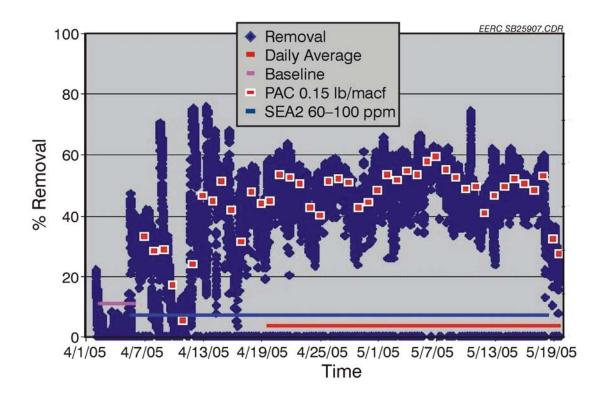


Figure 21. Mercury removal for extended testing at MRY using SEA2 and SEA2 with PAC.

preliminary on stack CMM measurements along with stack baseline measurements taken between the completion of the parametric testing and the start of the extended testing. Analyses of coal samples taken during the extended testing period will provide additional information on any variability in mercury concentration when completed. It should also be noted that the delivered cost of concentrated SEA2 increased significantly from when the testing was proposed. This, combined with the higher-than-expected injection rate required, meant that the SEA2 injection rate be the minimum necessary to achieve an estimated 55% mercury removal. This left little margin in case of changes in coal mercury level or fluctuations in pumping rate.

Testing of SEA2 only began April 5 and continued to April 19, 2005. During this period, problems were encountered with stratification of the diluted SEA2 solutions (a concentrated 50 wt/wt% SEA2 aqueous solution was diluted to a nominal 15 wt/wt% solution for injection). This dilution was a necessary consequence of the minimum pump capacity and the pump range. Further problems were experienced because of the quality of the delivered SEA2 solution, which was found to contain small quantities of oil, sludge, and organic debris. Significant scale formation was also encountered over the extended testing period, resulting in the plugging of filters, pumps, and flowmeters. For the SEA2-only portion of the testing, this resulted in erratic SEA injection and consequent fluctuations in the amount of mercury removed. Air agitation of the dilute SEA solution for 3 to 4 hours resulted well-mixed solutions, but sludge and scale formation were a recurring problem. Analysis of the scale has not been performed, but it is expected to show the scale to be common insoluble sulfates.

Injection of SEA2 in combination with a nominal 0.15-lb/Macf PAC injection was initiated April 19 and continued until May 18, 2005, when the supply of SEA2 was exhausted. PAC injection continued for several hours on May 19 after the SEA2 ran out in order to empty the PAC Super Sack feeding the PortaPac injection system.

During the SEA2-PAC injection, the 55% mercury removal target was exceeded 25% of the time, with removal rates as high as 65%; 50% of the time, the removal rate was between 50% and 55%.

4.2.7 Corrosion Probe Characterization – Conducted During the July – September 2005 Quarter

4.2.7.1 Introduction

To assess the BOP effects halogen-containing oxidation agents for mercury capture, six air-cooled corrosion test probes were installed at MRY. The probes were installed at the exit of the economizer (ECM), the air heater inlet (AHI), and the air heater outlet (AHO).

4.2.7.2 Probe Design

No standard test method was found in the literature appropriate for corrosion testing of tubing samples in a full-scale utility boiler environment; therefore, a customized testing procedure was developed. Each corrosion probe was designed to hold an 18-in.-long, 1-in.-diameter coupon consisting of a section of boiler tubing. To induce stress in the metal, the tubing is flattened in a 2-in. section at the midpoint to produce an oval with a minimum inside diameter of 0.5 in. The purpose of the flattening is to introduce stress in the metal to enhance potential corrosion.

The coupons are stainless steel. Two coupons for each location were fabricated by MRY personnel: a baseline coupon exposed to the normal flue gas environment and a test coupon exposed to flue gas while oxidation agents are being injected with the coal feed. Actual coupon outside diameter was 1 11/16 in. with a 0.25-in. wall. Reducing couplings were used to join the coupons to the probes.

The corrosion probe assembly is illustrated in Figure 22, and a picture of the coupon and cross-sectioned coupon is shown in Figure 23. The probe is inserted into the boiler through a 4-in. threaded pipe stub attached to the boiler wall. The threaded 4-in. pipe cap supports the probe. Welded to and extending through the pipe cap is a section of 1-in. Schedule 40 pipe. Stainless steel pipe was used for all of the probes. Additional couplings and 18-in. pipe lengths are screwed on to extend the probe length, with the test coupon held at the end. The test coupons are threaded for attachment to the corrosion probe assembly and for a pipe cap to seal the opposite end. A 0.5-in. 316 stainless steel tube runs the length of the probe. Compressed air for cooling is introduced through a pipe tee and flows down the annulus between tubing and probe pipe and back out the stainless steel tubing. A gate valve at the inlet is used to regulate the air flow, and a ball valve provides on/off control. Skin temperatures of the coupons are monitored



Figure 22. Picture of corrosion probe assembly.



Figure 23. Picture of coupon and cross-sectioned coupon.

with a thermocouple extending down the stainless steel tube and pressing against the end cap. A second thermocouple monitors exit cooling air temperature.

4.2.7.3 Coupon Testing

Baseline coupons were exposed to flue gas for 8 weeks, and long-term coupons were exposed to flue gas for 6 weeks, after which they were removed for analysis. On installation, uncooled coupon skin temperature was approximately 800°F at the ECM and 774°F at the AHI. Cooling airflow for the ECM coupon was set to maintain the coupon skin temperature at approximately 461°F, the AHI coupon were set to maintain the coupon skin temperature at approximately 485°F, and the AHO coupon temperature at approximately 272°F. Temperatures were logged with a computer at 5-minute intervals over the duration of the coupon testing. Note

that no feedback control of airflow based on temperature is used, so probe temperatures fluctuated somewhat based on flue gas temperature.

The baseline coupons were in the boiler from 11/18/04 with temperature data obtained from 16:34 to 1/17/05 with data collection ending at 13:12. The temperature profiles for the probes are shown in Figures 24–26. A summary of the temperature data for the baseline coupon testing is given in Table 1. Some temperature information was not obtained as a result of data "dropout" associated with the data logger, but was obtained each hour. During the period of 11/22/04 10:43 to 11/24/04 12:08, the compressed air supply to the AHO probe appears to have been reduced or interrupted, since the probe skin temperature was abnormally higher, and the exit cooling air temperature much lower than for the rest of the test period. At three brief periods between 11/30/04 and 12/13/04, both the probe skin temperature and exiting cooling air temperature went much lower than normal and the probe skin temperature was close to the temperature of its cooling air, indicating either reduced/interrupted flue gas or excess cooling air to the ECM and AH probes in these periods.

The long-term test coupons were tested from 4/5/05 to 5/17/05. However, most of the probe temperature data were lost as a result of computer hard disk failure. The temperature data were retained only for the period of 4/11/05 7:03 to 4/15/05 5:19. The probe temperature profiles of this period are shown in Figures 27–29. A summary of the temperature data for this period of testing is given in Table 2. The probe temperatures in this short period were fairly stable.

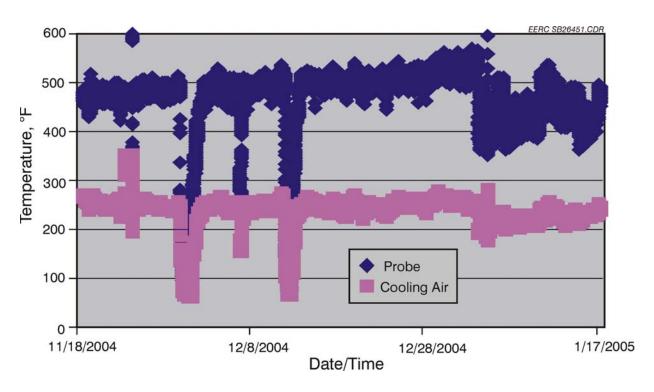


Figure 24. MRY ECM baseline probe temperature profile.

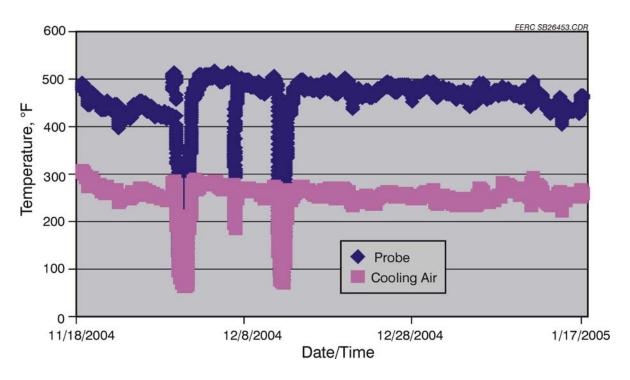


Figure 25. MRY AHI baseline probe temperature profile.

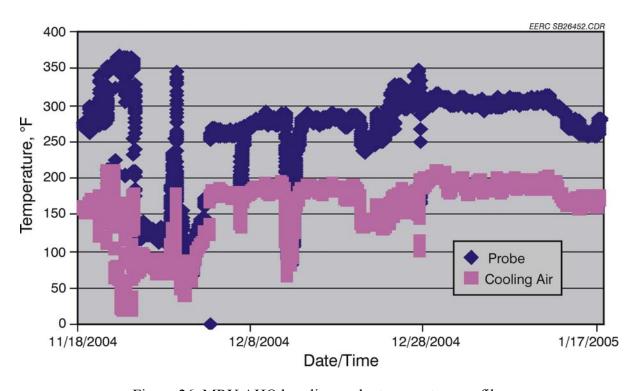


Figure 26. MRY AHO baseline probe temperature profile.

Table 1. Baseline Probe Temperature, °F

		,				
		ECM				AHO
		Cooling		AHI Cooling	AHO	Cooling
	ECM Probe	Air	AHI Probe	Air	Probe	Air
Av	472.2	235.3	453.3	250.0	260.9	158.0
Min.	66.4	58.7	66.6	59.1	55.1	16.3
Max.	878.3	353.3	517.5	307.7	368.7	209.8
Std. Dev.	97.6	38.2	73.4	35.5	65.9	44.3

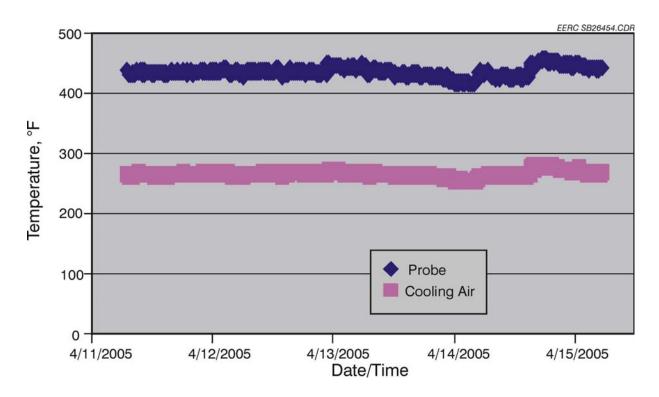


Figure 27. MRY ECM long-term probe temperature profile.

4.2.7.4 Coupon Analysis

To preserve any ash deposit adhering to the probes, they were wrapped in plastic film and placed in cardboard tubes prior to transport. Upon arrival at the EERC, the test coupon sections of the probes were sprayed with a mixture of acetone and epoxy to affix the ash deposits during subsequent cutting. The test coupons were cross-sectioned with a metal band saw at the midpoint of the crimped area. The cutting operation was performed without lubrication to prevent contamination of the coupons. The samples were then mounted in epoxy and polished to obtain samples for scanning electron microscopy (SEM) analysis.

All of the six coupon samples were examined by SEM to ascertain the degree of corrosion at the metal-metal oxide-deposit interface. Line scans were performed for each sample on one of the curved sections and one of the flat sections. Four lines were selected at each location for

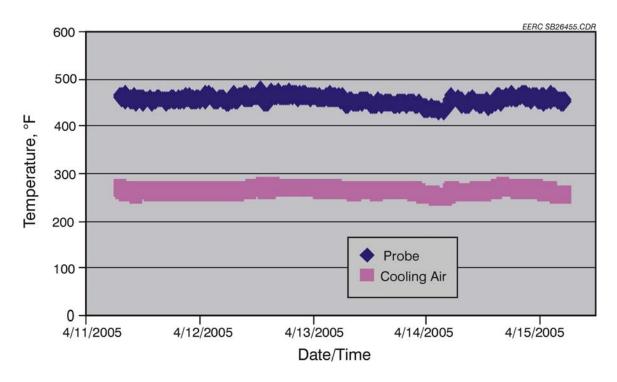


Figure 28. MRY AHI long-term probe temperature profile.

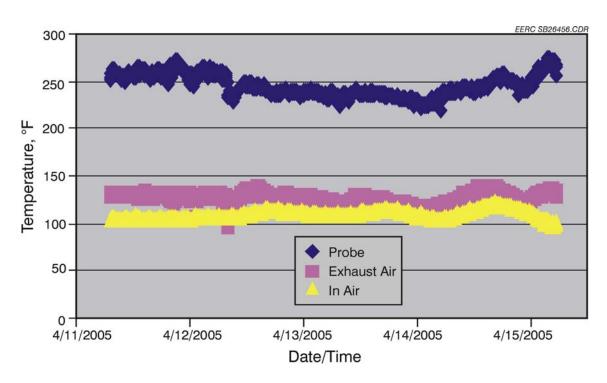


Figure 29. MRY AHO long-term probe temperature profile.

Table 2. Long-Term Probe Temperature, °F

	ECM	ECM in	AHI	AHI Exh.	AHO	AHO	AHO in
	Probe	Air	Probe	Air	Probe	Exh. Air	Air
Av	435.7	266.1	456.0	264.4	245.3	127.2	109.0
Min.	414.3	252.7	430.7	250.0	220.1	97.4	97.5
Max.	457.0	281.2	478.7	276.8	274.6	138.9	121.3
Std. Dev.	8.1	4.9	8.2	4.7	11.5	5.0	4.2

quantitative point analyses for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Fe, Ni, Mn, and O. Each line covers 40 µm long across the metal–metal oxide–deposit interface, and 81 point analyses were done along the line in equal intervals between points.

4.2.7.4.1 Economizer Coupons

Figure 30 shows the appearance of typical areas of the steel—oxide interface for the curve and flat sections of the ECM baseline and long-term coupons. The bright area at the right of each picture is the steel; the gray area is the surface oxide layer, and the black area at the left is the epoxy in which the coupon section is mounted. For both the baseline and long-term samples, a portion of the deposit is seen as closely packed gray spheres at the left of the pictures. The baseline coupon sample has a smooth steel surface, while the long-term test coupon sample has a rough steel surface, indicating more extensive corrosion of the long-term test coupons. On the flat section, the baseline sample shows a thicker layer of deposit than the long-term sample.

Figures 31 and 32 give typical results of SEM line scan analyses for iron, chrome, nickel, sulfur, sodium, potassium, calcium, silicon, and aluminum for the economizer coupons. Some analysis points outside of the iron oxide interface and deposit layer reported high chlorine contents. This is caused by the sample-mounting material, which is chlorine-based epoxy. Results of the four line scans on each of the curve and flat sections of the economizer coupons are very similar, and two sets of baseline and long-term testing are presented in the plots.

The line scans show a decrease in iron content going from the tube metal to the oxide layer. The deposits also show significant iron content resulting from iron-rich fly ash particles. Both the baseline and long-term coupons have high levels of sulfur in the oxide and deposit layers. On the flat section, the deposits on the long-term coupon have much higher sulfur content than the deposits on the baseline coupon. On the curve section, the sulfur contents in the deposits on the baseline and long-term coupons are not significantly different. It seems that sulfur is the primary oxidation agent causing the coupon corrosion.

Aluminum, silicon, and calcium are the major elements comprising the deposits on the coupons. The deposits on the baseline coupon have relatively higher aluminum and silicon contents than the deposits on long-term coupons, while the deposits on the long-term coupon have much higher calcium content than the deposits on baseline coupons, especially on the curve section. This suggests that some increase in calcium sulfate deposition is occurring as a result of the SEA2 addition in long-term test.

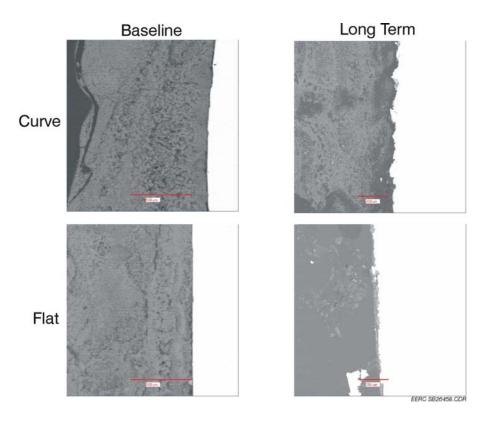


Figure 30. Backscattered electron image of MRY ECM coupons.

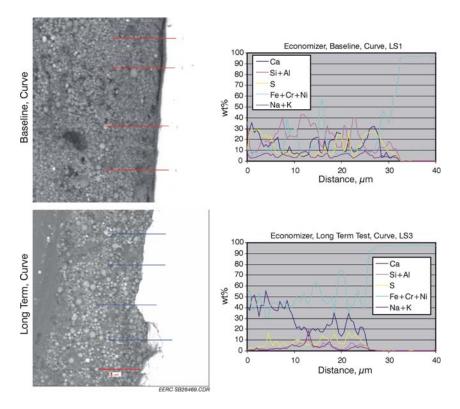


Figure 31. Comparison of ECM baseline and long-term coupons.

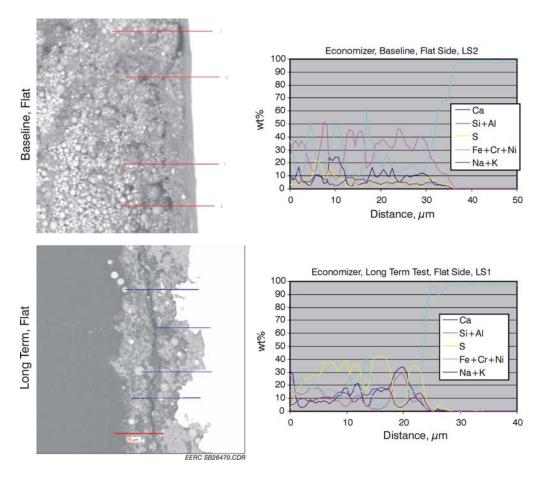


Figure 32. Comparison of ECM baseline and long-term coupons.

4.2.7.4.2 AHI Coupons

Figure 33 shows the appearance of typical areas of the steel—oxide interface for the AHI baseline and long-term coupons. The bright area at the right of each picture is the steel, the gray area is the surface oxide layer, and the black area at the left being the epoxy in which the coupon section is mounted. Note that the photographs of the AHI coupons are similar to that of the economizer coupons shown in Figure 30, the baseline coupons have a smooth steel surface, and the long-term coupons have a rough steel surface, indicating more intensive corrosion of long-term coupons. The deposit layers, however, are much thinner than that of economizer coupons. The long-term deposits are closely packed on the steel surface, while there is a "crack" between the deposit layer and the steel surface on baseline coupons.

The results of SEM line scan analysis giving Fe, Cr, Ni, S, Na, K, Ca, Al and Si concentrations for the AHI coupons are shown in Figures 34 and 35. In general, these results are similar to those seen for the ECM coupons. A notable difference is that the deposits on long-term coupons have much higher Na, K, and S concentrations. On the flat section of the long-term coupon, the deposit layer is composed of pure Na, K, and Ca sulfates, without aluminosilicate fly ash and iron-rich particles. The total Na and K concentration is as high as over 40% in some

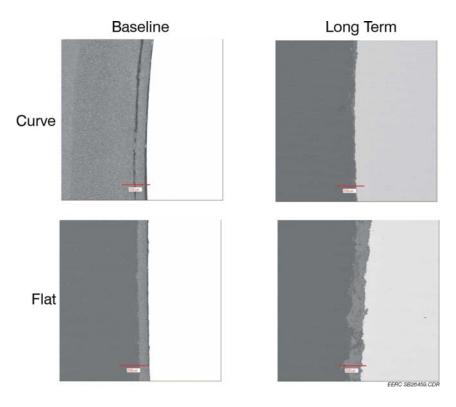


Figure 33. MRY AHI coupons.

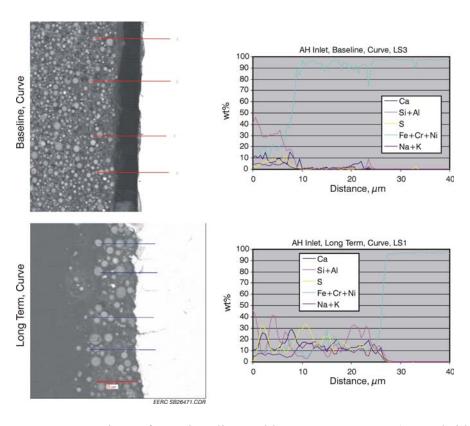


Figure 34. Comparison of AHI baseline and long-term coupons (curved side).

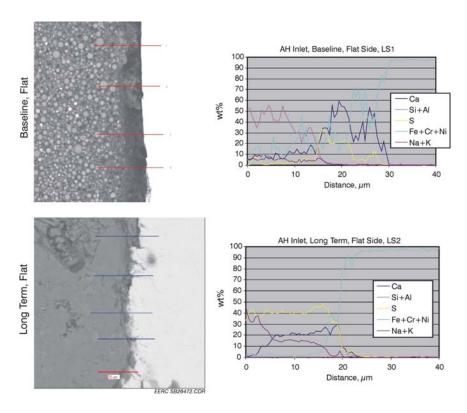


Figure 35. Comparison of AHI baseline and long-term coupons (flat side).

parts of the deposit layer. The analysis results do not clearly show increased Ca concentration in the long-term deposit layer.

4.2.7.4.3 AHO Coupons

Figure 36 shows the appearance of typical areas of the steel—oxide interface for the AHO baseline and long-term coupons. The bright area at the right of each picture is the steel, the gray area is the deposit layer, and the black area at the left being the epoxy in which the coupon section is mounted. The deposit layer on the baseline coupon is much thicker than that of the long-term coupon. Unlike the ECM and AHI coupons, the steel surfaces the AHO baseline and long-term coupons look similar. The long-term coupon steel surface is not as rough as that of the ECM and AHI long-term coupons. There is no indication of more intensive corrosion of the long-term coupon than the baseline coupon.

The results of SEM line scan analyses giving Fe, Cr, Ni, S, Na, K, Ca, Al, and Si concentrations for the AHO coupons along with the micrographs of the scanned area are shown in Figures 37 and 38. It is interesting that the deposit layer on the curve is different from that on the flat section of the same coupon. On the baseline coupon, although both the curve and flat sections have a deposit layer of aluminosilicate fly ash particles cemented by Na, K, and Ca sulfates, the fly ash particles at the curve are submicrometer to about 2 μ m in diameter, while the particles at the flat sections are much coarser, up to over 30 μ m in diameter. On the long-term coupon, the deposit layer of the flat section is composed of fine aluminosilicate particles

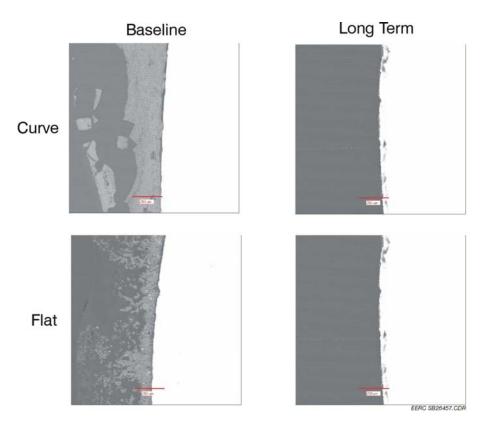


Figure 36. MRY AHO coupons.

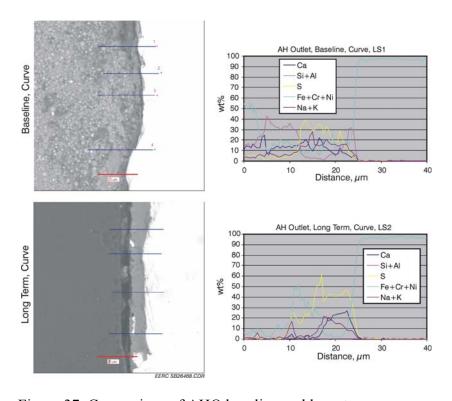


Figure 37. Comparison of AHO baseline and long-term coupons.

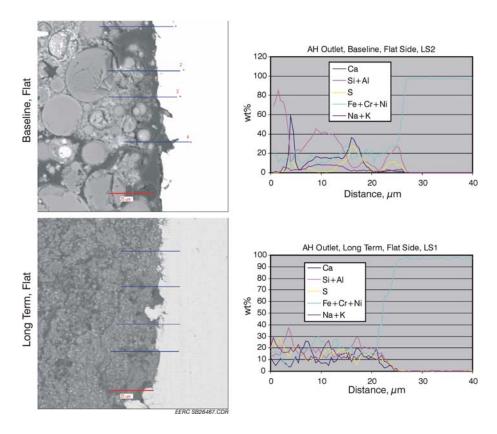


Figure 38. Comparison of AHO baseline and long-term coupons.

cemented with Na, K, and Ca silicate, while the deposit on the curve is a thin layer of Na, K, and Ca sulfates, without aluminosilicate particles found.

Chemically, these results are similar to those seen for the ECM and AHI coupons. The long-term deposit has higher Na, K, and S concentrations and lower Al and Si concentrations than the baseline deposit. On the curve, the long-term coupon has higher Ca in the deposit layer than the baseline coupon, while on the flat section, this phenomenon is not well held. It is hard to conclude that expositing SEA2 has increased Ca sulfate deposition on the long-term coupon.

4.3 Results from Monticello Testing

4.3.1 Experimental – Summary of Activities Conducted During the October – December 2005 Quarter

Full-scale boiler halogen injection tests were performed at MoSES Unit 3 to evaluate mercury oxidation and removal across a cold-side ESP/wet FGD system. Short-term parametric tests were followed by two 2-week continuous injection tests. Parametric tests evaluated calcium chloride (CaCl₂) and calcium bromide (CaBr₂). Based on the results, CaBr₂ was selected for the long-term tests. The halogen was introduced to the boiler via a metered salt solution that was sprayed onto the coal as it fell off the weigh belt and into the pulverizers. EPRI semicontinuous

mercury analyzers measured the resulting changes in flue gas mercury concentration and speciation.

Other gas-sampling measurements included the OH method and the sorbent tube method for flue gas mercury concentrations and Methods 26 and 26A for flue gas halogen concentrations. Process samples, such as coal, fly ash, and FGD by-products, were collected for analysis. Appendix A summarizes the sample times for the collected flue gas and plant process samples. Plant process data were also collected. These data will be used to evaluate the balance of plant impacts of halogen addition. The data will also be used to perform an economic evaluation of the process for mercury control.

This chapter describes the experimental plan for the project. First, pertinent design details of the host site are provided. Then, the chemical injection process and injection equipment design are described. The flue gas sampling methodology and unit process sample methodology are discussed. Finally, the executed schedule of testing is listed.

4.3.1.1 Host Site Description

TXU Energy's MoSES Unit 3 was the host site for this test program. Unit 3 fires a blend of approximately 50% Texas lignite and 50% PRB and is rated at 793 MW. Figure 39 illustrates the Unit 3 configuration. Unit 3 has a horizontally opposed, pulverized coal boiler with low-NO_X burners. A moderately large (design SCA of 452 ft²/kacfm) cold-side ESP is used for particulate control, and a limestone forced oxidation spray tower FGD system is used for SO₂ control. Three spray absorbers achieve about 90% SO₂ removal on the flue gas treated. About 50% of the flue

Air Heaters

Air Heaters

Scrubbers

Scrubbers

Stack

Boo-MW

Boiler

Electrostatic

Precipitators

EERC CC26735.CDR

Figure 39. Schematic of MoSES Unit 3 configuration.

gas is bypassed. The ESP outlet flue gas typically contains about 25% Hg^{+2} and 75% Hg^{0} , with total Hg concentrations of about 20 $\mu g/Nm^{3}$.

4.3.1.2 Selection of Halogen Addition Method

There are three possible ways to add a halogenated material to the boiler: 1) add dry salt to the coal, 2) spray salt solution onto the coal, and 3) inject salt solution directly into the boiler. The method selected for these tests was spraying of the salt solution onto the coal. This method was chosen because the spray solution can be applied to the coal as it enters the pulverizers, thereby limiting the time between salt application and boiler entrance to a few seconds. With this method, the entire boiler will be treated with the halogen material.

The dry addition method was not chosen for various reasons. At MoSES, the dry addition method might have been applied at the coal handling yard, in which case up to 6 hours would have elapsed between addition of the salt material and injection into the boiler. This time delay would have made on-the-fly changes to the salt injection rate infeasible. Alternatively, the dry coal might have been added to the furnace pipes as the coal enters the furnace. However, this method of application would entail pneumatic transport of the salt, which can be difficult with the deliquescent materials.

The spraying of halogen material directly into the boiler was not chosen. In previous EPRI-funded testing, it has been difficult to feed salt solution into the boiler for prolonged periods of time without plugging the injection lances. The salt spray from the lances has a tendency to blow back onto the lances and plate onto them. For the 2-week continuous injection tests, the boiler addition method appeared too risky.

4.3.1.3 Injection Equipment

Liquid salt injection equipment for the Monticello chemical injection tests included chemical holding tanks, a pump skid, hose, and injection lances. The salt solution was stored in plastic holding tanks (Figure 40). Four double-walled tanks were used for this project, each holding approximately 2500 gal.

The injection skid (Figure 40), which includes two pumps and all associated flow indication/control equipment was provided by DOE. The physical dimensions of the skid were 80 in. long by 60 in. wide by 75 in. high, with a weight of 1800 lb. The skid was equipped with two pumps, each pump with a pumping capacity of 0.1 to 2.2 gal/min with a maximum pressure of approximately 80 psi. The power requirements for the pump skid were 480 volt, 3 phase.

The control system for the pump skid contained a signal generator producing a 4–20 ma signal that corresponded to the desired ppm feed rate. A second 4–20 ma signal was obtained from the plant computer that corresponded to the coal feed rate for the unit. A programmable logic controller (PLC) compared the two signals and generated a signal to control the variable frequency drives for the pumps to maintain a constant additive to the coal feed rate. A flowmeter at the pump outlet provides feedback to the PLC as to the actual flow rate. In addition, a





Figure 40. Chemical storage tanks and pump skid for MoSES Unit 3 tests.

rotameter was installed for each pump outlet to provide visual and quantitative verification of the fluid flow rate.

Injection skid data logged by the plant's data logger included the flow rates for each pump and the coal feed rates for each pulverizer (other unit process data are discussed later in this section). The following injection skid data were logged periodically by the URS process engineer: flow rates measured by the rotameters and positive displacement flowmeter, tank level, and other parameters that were related to the maintenance of the injection skid. Samples of the injected salt solution were taken daily so that they could be analyzed for halogen concentration. These measured values will be used in conjunction with the salt flow rate to determine the amount of halogen added to the furnace.

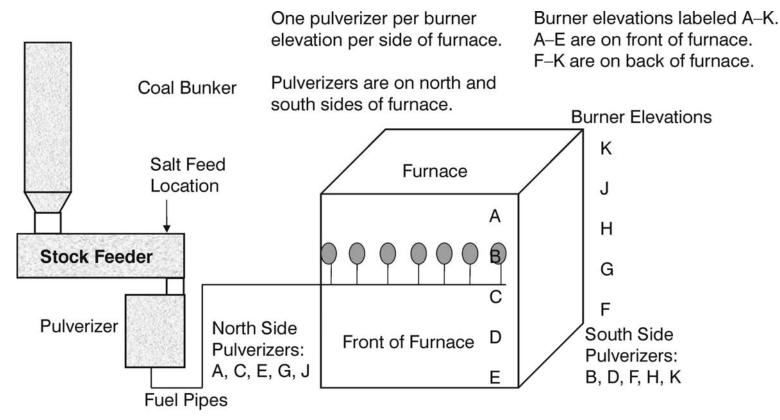
The salt solution was pumped through a hose to the stock feeder (Figure 41) for the pulverizer, which was located at approximately 60 feet elevation. The liquid exited a stainless steel tube inserted into the top of the stock feeder (Figure 41) and fell onto the coal in the stock feeder as it fell off the weigh belt. The coal and salt solution mixed together in the pulverizer and then traveled through the fuel pipes to the furnace.

Figure 42 shows the coal feeding system for the furnace, from the coal bunkers to the furnace fuel pipes. The front side of the furnace has five burner elevations, labeled A, B, C, D, and E. The back side of the furnace has five corresponding elevations, labeled K, J, H, G, and F. Each elevation on each side is served by its own coal bunker, stock feeder, and pulverizer.





Figure 41. Stock feeder deck (top) and insertion of halogen feed line into top of stock feeder for MoSES Unit 3.



Choose to feed salt to pulverizers on only north or south side; choose one pulverizer that serves front of furnace and one that serves back of furnace. For example, feed pulverizers E and J or D and K.

EERC CC26736.CDR

Figure 42. MoSES coal handling system layout.

The stock feeder is located between the coal bunker and the pulverizer. The residence time of the coal from the stock feeder to the furnace is only a few seconds. Good mixing of the salt solution and the coal is achieved in the pulverizer. Each pulverizer feeds seven fuel pipes that span the width of the furnace. The pulverizers are located on the north and south sides of the furnace. Pulverizers on the south side of the furnace feed both the back and front sides of the furnace; likewise for the north side.

The stock feeders used in this test program were chosen for their proximity to each other; that is, all stock feeders were situated on the north side of the furnace. The stock feeders were also chosen to ensure that the salt was applied to coal being fed to both the back and front walls of the furnace. The salt was sprayed as a liquid on to the coal into stock feeders B, D, F and H for the parametric tests. For the long-term tests, because of the small amount of solution to be pumped, only feeders B and H were used.

4.3.1.4 Flue Gas Sampling

An integral part to this test program is the collection and analysis of gas, solid, and liquid samples. Flue gas mercury concentrations (total and elemental mercury) were measured at the ESP inlet, ESP outlet, and FGD outlet using EPRI semicontinuous emission monitors (SCEMs). Flue gas mercury concentrations were also made with the OH method, Appendix K method, and a modified sorbent tube method at various times in the test program. Flue gas halogen concentrations (HCl, HBr, Br₂, and Cl₂) were measured with Method 26 (mini impinger method) at the ESP inlet and with Method 26A at the FGD outlet.

Table 3 indicates the frequency with which the flue gas sampling occurred. Appendix A summarizes the specific dates and times for each flue gas sample that was collected. The OH method, Appendix K method, and Methods 26 and 26A are standard methods. The SCEM mercury analyzer is an experimental method developed by EPRI and described below.

4.3.1.4.1 Mercury SCEMs

Flue gas vapor-phase mercury analyses were made using EPRI semicontinuous analyzers depicted in Figure 43. At each sample location, a sample of the flue gas is extracted at a single point from the duct and then drawn through an inertial gas separation (IGS) filter to remove particulate matter. This IGS filter consists of a heated stainless steel tube lined with sintered material. A secondary sample stream is pulled across the sintered metal filter and then is directed through the mercury analyzer at a rate of approximately 1–2 L/min thus providing near real-time feedback during the various test conditions. The analyzer consists of a cold-vapor atomic absorption spectrometer (CVAAS) coupled with a gold amalgamation system (Au-CVAAS). Since the Au-CVAAS measures mercury by using the distinct lines of the UV absorption characteristics of elemental mercury, the nonelemental fraction is converted to elemental mercury prior to analysis using a chilled reduction solution of acidified stannous chloride. Several impingers containing alkaline solutions are placed downstream of the reducing impingers to remove acidic components from the flue gas; elemental mercury is quantitatively

Table 3. Frequency of Flue Gas Sampling Methods at MoSES Unit 3

Flue Gas Sampling	Sampling	Frequency of I	Measurement
Method	Location	Parametric Tests	Long-Term Tests
Mercury SCEM	ESP Inlet,	Semicontinuous	Semicontinuous
	ESP Outlet,		
	Scrubber Outlet		
OH Method	ESP Inlet	Two sets during BL	One set of three
OH Method	ESP Outlet	Two sets during BL	None
OH Method	FGD Outlet	None	One set of three
Method 26A	FGD Outlet		One set of three
Method 26	ESP Inlet	Once per injection	Twice per day
		rate	
Appendix K	U3 Stack	None	Periodic
Modified Sorbent	ESP Inlet	None	Periodic
Tube Method			
Modified Sorbent	FGD Outlet	None	Periodic
Tube Method			

transferred through these impingers. Gas exiting the impingers flows through a gold amalgamation column where the mercury in the gas is adsorbed (<60°C). After adsorbing onto the gold for a fixed period of time (typically 1 min), the concentrated mercury is thermally desorbed (>400°C) in nitrogen or air, and flows as a vapor stream to a CVAAS for analysis. Therefore, the total flue gas mercury concentration is measured semicontinuously with a 1-min sample time followed by a 2-min analytical period.

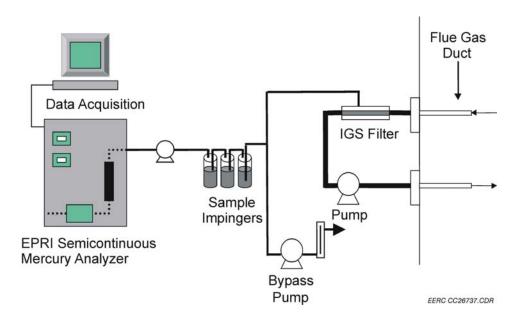


Figure 43. Schematic of the EPRI semicontinuous mercury analyzer used to measure mercury in situ during the MoSES Unit 3 tests.

To measure elemental mercury only, an impinger containing either 1 M potassium chloride (KCl) or 1 M Tris Hydroxymethyl (aminomethane) and EDTA is placed upstream of the alkaline solution impingers to capture oxidized mercury. Oxidized forms of mercury are subsequently captured and maintained in the KCl or Tris impingers while elemental mercury passes through to the gold amalgamation system. Comparison of "total" and "elemental" mercury measurements yields the extent of mercury oxidation in the flue gas.

Appendix B describes how vapor-phase mercury concentrations are calculated from the data recorded by the SCEMs.

4.3.1.5 Process Sampling

Process samples included coal, ESP ash, FGD slurry, FGD makeup water, limestone, and the injected salt reagent solution. Care was taken to obtain representative samples of the process samples. URS was responsible for obtaining all of these process samples, except for the coal which was gathered by the unit operators. The target analytes for each process sample are listed in Table 4. Appendix A lists the dates and times for all process samples that were collected. Not all collected samples were analyzed, rather, periodic samples were selected to represent the operation of the process across the duration of the test program. The sample collection method and sample frequency were specific to each process sample type.

4.3.1.5.1 Coal

The PRB and Texas lignite coals were sampled and analyzed separately. At Monticello, the only location available for segregated coal samples is at the coal belt in the coal feed yard, which is approximately 6 hours upstream of the furnace. Coal samples were collected once per day.

4.3.1.5.2 Ash

Fly ash was collected and analyzed by hopper from the Unit 3 B ESP, which was the ESP across which flue gas mercury measurements were made. Figure 44 shows the hopper layout for the B-side ESP on Unit 3. There are five rows of hoppers in the ESP; however, ash

Table 4. Target Analytes for Solid and Liquid Process Samples

Tubic it Tui get illiui j	able is full got finally too for both and find it to copy build be				
Process Sample	Target Analytes				
Texas Lignite Coal	LOI, Hg, halogens, ultimate/proximate				
PRB Coal	LOI, Hg, halogens, ultimate/proximate				
ESP Ash	LOI, Hg				
FGD Solids	Hg, wt% solids, % inerts, Ca^{2+} , Mg^{2+} , SO_3^{2-} , SO_4^{2-} , CO_3^{2-}				
FGD Liquors	Hg, wt% solids, % inerts, Ca ²⁺ , Mg ²⁺ , SO ₃ ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ Hg, SO ₃ ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , Cl, Ca ²⁺ , Mg ²⁺ , Na ⁺				
Limestone	Hg, purity				
Makeup Water	Hg				

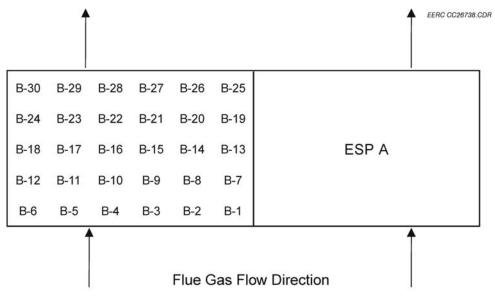


Figure 44. Hopper Diagram for Unit 3B ESP.

samples were collected only from the first two rows (Hoppers B-1 through B-12). The final three rows of the ESP did not yield an appreciable amount of ash for collection.

During the parametric tests, ash samples were collected at the end of each injection test period. The ESP hoppers are continually emptied at Monticello, so the ash collected at the end of the injection test period was representative of the ash collected by the ESP during the test period. During the continuous injection tests, ash samples were gathered once per day.

4.3.1.5.3 Scrubber Samples

Scrubber samples were taken by URS personnel from the exit of the slurry recirculation pump on the C scrubber module on Unit 3. The FGD sampling included a slurry to be filtered for mercury analysis of solids and liquid. The sample was filtered on-site within an hour of collection to ensure that the mercury did not repartition between the solid and liquid phases. A full set of diluted filtrates (DFs) was taken each day. DFs are used to preserve the liquid sample for analysis of SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , halogens, Ca^{2+} , Mg^{2+} , and Na^+ . A slurry sample was taken each day and filtered off-site at URS-Austin for weight % solids and cations and anions in the solids $(Ca^{2+}, Mg^{2+}, SO_3^{2-}, SO_4^{2-}, and CO_3^{2-})$.

The scrubber was sampled during the baseline periods of operation and once per day during the long-term tests. The scrubber was not sampled during the parametric injection test periods, as these test periods were too short in comparison to the residence time of the slurry in the scrubber. Therefore, it would not have been possible to obtain representative slurry samples during the parametric tests.

4.3.1.5.4 Limestone and Makeup Water

The limestone reagent feed and makeup water were sampled once during the test program.

4.3.1.5.5 Plant Process Data

Process data typically archived by the plant were monitored to determine if any correlation exists between changes in mercury concentration with measured plant operation. The process data will be used to determine any balance-of-plant effects, such as air heater plugging or ESP operation. Process data collected by the plant are summarized in Table 5. URS engineers coordinated with plant personnel to retrieve the necessary historical plant operating data files.

Table 5. Process Data to be Collected at MoSES

Parameter	Sample/Signal/Test
Coal	Plant signals:
	- Coal feed rate, ton/hr
	 Coal analysis data, especially lb/MMBtu, % ash
	 Fraction of PRB and TxL feed by weight
Unit Operation	Plant signals:
	 Boiler load, gross MW
	– Heat rate, gross Btu/kwh
	 Boiler steam flow, temperature, and pressure
	- Furnace O ₂
Temperatures	Plant signal at air heater inlet, air heater outlet, ESP outlet
Air Heater Operations	Air heater pressure drops, in. H ₂ O for gas and air sides
ESP Operations	Plant data:
-	 ESP power, current, voltage by field
	 Rapping frequency
	– ESP design specs.
	 Sparking and arcing data
FGD Operations	Plant Data:
	– pH
	− SO ₂ inlet conc.
	– SO ₂ removal
	 Reagent flow rate
	Slurry density
	– ME flow rate
	– ME delta P
	– ME makeup flow
	Oxidation air flow
	– Blowdown rate
	 Makeup water flow
	 Inlet pressure
	Pond return flow
	 Transition duct makeup water flow
Stack Data	Plant signals:
	$-NO_{x}$ (CEM)
	$-SO_2(CEM)$
	$-O_2$ or CO_2
	- Opacity
	– Flow rate

4.3.1.6 Test Schedule

The test program duration was approximately 2 months. Table 6 provides the dates of the key phases of the test program.

Mercury SCEM measurements were made during all the key phases of the test program. Table 7 provides the dates of other manual sampling methods that were performed at Monticello Unit 3, including the OH method, Method 26, and Appendix K method. A detailed table with specific sample times for all gas characterization methods and process samples is provided in Appendix A.

Table 6. Dates of Key Phases of Completed Test Program

Start Date/Time	End Date/Time	Test Activity
10/24/05	10/26/05	Baseline measurements
10/27/05	10/28/05	CaCl ₂ parametric tests
10/29/05	10/30/05	CaBr ₂ parametric tests
11/1/05 17:00	11/5/05 12:15	Baseline measurements
11/5/05 12:15	11/18/05 18:50	CaBr ₂ continuous injection test
		(target rate of 50 ppm AR ¹ in coal)
11/18/05 18:50	11/19/05 8:45	Baseline measurements
11/19/05	11/28/05	Break between first and second CaCl ₂
		continuous injection tests
11/28/05 17:00	12/2/05 11:10	Baseline measurements
12/2/05 11:10	12/12/05 11:39	CaBr ₂ continuous injection test
		(target rate of 100 ppm in coal)
12/12/05 11:39	12/14/05 14:20	CaBr ₂ continuous injection test
		(target rate of 200 ppm in coal)
12/14/05 14:20	12/15/05 14:44	Baseline measurements
12/15/05 14:44	12/16/05 14:37	Iodide parametric tests

¹ Active reagent.

Table 7. Dates of Manual Measurement Efforts

Date*	Test Activity	Sample Locations
10/25/05	OH method, set 1	ESP inlet, ESP outlet
10/26/05	OH method, set 2	ESP inlet, ESP outlet
11/16/05	OH method, set 3	ESP inlet, FGD outlet
11/17/05	M26A	ESP inlet, FGD outlet
Periodically through	M26	ESP inlet
entire test program		
11/8/05 - 11/11/05	Appendix K (performed by TXU)	Stack
11/14/05 - 11/18/05	Appendix K (performed by TXU)	Stack
Periodically through	Modified sorbent tube method	ESP inlet, FGD outlet
entire test program		

^{*} Specific sample times for individual runs can be found in Appendix A.

4.3.2 Results and Discussion – Summary of Activities Conducted During the January – March 2006 Quarter

This update covers the reporting period from January 1, 2006, through March 31, 2006. During this quarter, samples and data collected during the chemical injection tests were analyzed from the tests conducted at MoSES Unit 3.

Full-scale boiler halogen injection tests were performed at MoSES Unit 3 to evaluate mercury oxidation and removal across a cold-side ESP/wet FGD system in a Texas lignite-derived flue gas stream. Short-term parametric tests were followed by two 2-week continuous injection tests. Parametric tests evaluated CaCl₂ and CaBr₂. Based on the results, CaBr₂ was selected for the long-term tests. The long-term tests were executed as two 2-week periods of CaBr₂ injection. Baseline measurements were made prior to the start of each long-term period. In the first 2-week period, the target injection rate was 50 ppm Br equivalent in the dry coal; for the second 2-week period, the primary target injection rate was 100 ppm Br equivalent in the dry coal. Table 8 summarizes the test schedule for the parametric tests, indicating the times at which each injection rate was tested.

Table 8. Executed Test Schedule for Parametric Tests at MoSES Unit 3

			Targeted Injection
Start			Rate,
Date/Time	End Date/Time	Test Activity	ppm AR in the coal
10/24/05	10/27/05 12:55	Baseline	0
10/27/05 12:55	10/27/05 17:05	CaCl ₂ injection	600
10/27/05 17:05	10/28/05 10:29	Baseline	0
10/28/05 10:29	10/28/05 14:00	CaCl ₂ injection	400
10/28/05 14:00	10/28/05 18:02	CaCl ₂ injection	800
10/28/05 18:02	10/29/05 10:39	Baseline	0
10/29/05 10:39	10/29/05 14:40	CaBr ₂ injection	100
10/29/05 14:40	10/29/05 18:00	CaBr ₂ injection	200
10/29/05 18:00	10/30/05 12:00	Baseline	0
10/30/05 12:00	10/30/05 15:27	CaBr ₂ injection	12
10/30/05 15:27	10/30/05 16:14	CaBr ₂ injection	25
10/30/05 16:14	10/30/05 18:20	CaBr ₂ injection	50
10/30/05 18:20	10/30/05 19:10	CaBr ₂ injection	100

4.3.2.1 Baseline Test Results

Baseline flue gas mercury measurements were made during three distinct periods in the test program. These baseline periods are as follows:

• October 24, 19:50, through October 27, 12:55. These are the days prior to the parametric tests. Data for this time period are shown in Figure 45.

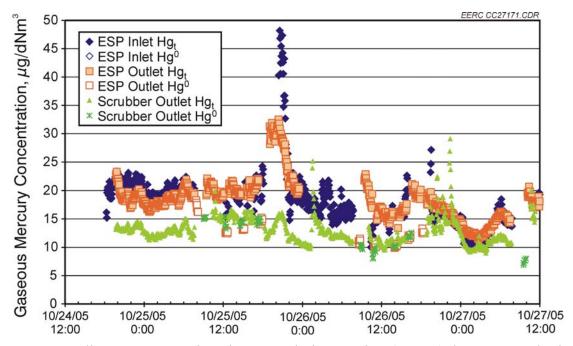


Figure 45. Baseline mercury semicontinuous emission monitor (SCEM) data measured prior to parametric mercury control injection tests at MoSES Unit 3.

- November 1, 17:00, through November 5, 12:15. These are the days prior to the first long-term injection test. Data for this time period are shown in Figure 46.
- November 28, 17:00, through December 2, 11:10. These are the days prior to the second long-term injection test. Data for this time period are shown in Figure 47.

The total gas-phase mercury concentration was highly variable at MoSES Unit 3, with the baseline ESP inlet total mercury concentration ranging between 10 and 50 μ g/Nm³; however, the concentrations were typically between 15 and 30 μ g/Nm³ over the course of the baseline test days. The ESP inlet and outlet mercury was typically present as 10%–40% oxidized mercury; however, oxidized mercury levels as high as 55% were observed December 1–2, 2005. Calculated baseline mercury removal across the ESP ranged from –10% to 10%; therefore, removal of mercury across the ESP was negligible overall. The removal of mercury across the ESP/FGD system was equivalent to the mercury removal across the FGD ranged from 10% to 60% over the course of the baseline testing; however, the mercury removal across the ESP/FGD system was more typically 10%–40%. The measured mercury removal across the FGD agreed well with the ESP outlet oxidation.

The baseline HCl/Cl_2 and HBr/Br_2 concentrations were measured with Method 26 during various baseline periods. The average results are tabulated in Table 9. Results from individual runs are summarized in Appendix C. The chlorine and bromine species were below the detection limits of the method (0.06 and 0.01 ppm, respectively). The baseline HCl concentration ranged from 1.3 to 5.6 ppm, with an average of 3.0 ppm. The baseline HBr concentration was 0.06 ppm.

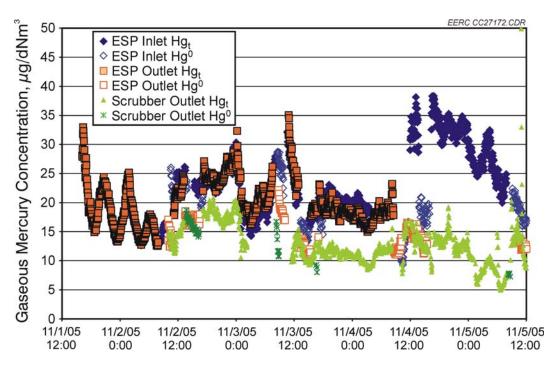


Figure 46. Baseline mercury SCEM data measured prior to the first set of long-term mercury control injection tests at MoSES Unit 3.

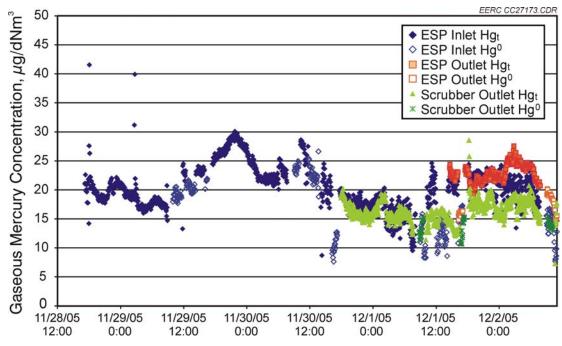


Figure 47. Baseline mercury SCEM data measured prior to the second set of long-term mercury control injection tests at MoSES Unit 3.

Table 9. Average Baseline Flue Gas Halogen Concentrations at MoSES Measured with Method 26

	Cl ₂ ,	HCl,	Br ₂ ,	HBr,
	ppm, dry, 3% O ₂			
Baseline	< 0.06	2.97	< 0.01	0.06

4.3.2.2 Parametric Test Results

Two salt solutions were evaluated in parametric tests: CaCl₂ and CaBr₂. Each salt solution was tested at multiple injection rates over 2-day periods. Flue gas mercury concentrations were monitored continuously with mercury SCEMs at the ESP inlet, ESP outlet, and FGD outlet. Method 26 measurements were made at the ESP inlet during each parametric test condition to verify the amount of halogen species present in the flue gas.

Tables 10 and 11 show the measured flue gas HCl/Cl₂ and HBr/Br₂ concentrations during the parametric test periods. The data presented are the average of multiple runs conducted at each test condition (data for individual runs are listed in Appendix C). The measured Cl₂ and Br₂ concentrations were less than the detection limits of 0.08 and 0.01 ppm, respectively.

The theoretical flue gas halogen (as HX) concentrations shown in Tables 10 and 11 were computed from the actual halogen injection rate and an estimated flue gas flow rate. The flue gas flow rate was estimated from an EPA Method 19 F-factor calculation. For the theoretical calculation, it was assumed that all of the injected halogen (X) converted to HX in the flue gas. The calculation of the theoretical HX concentration included the baseline measurement of HX.

The measured flue gas HCl concentration correlates well with theoretical predictions, with the measured flue gas HCl concentration ranging from 92% to 97% of theoretical. For the CaBr₂ tests, the measured HBr concentrations were closest to the theoretical concentrations at the lowest injection rates of 12.5 and 50 ppm Br equivalent in the coal (dry basis). At the higher injection rates of 100 and 200 ppm Br equivalent in the coal, the flue gas HBr concentration is approximately 60% of the theoretical value. This same trend of comparison between the measured to theoretical HBr concentrations was seen in the 2-week continuous tests.

Table 10. Comparison of Measured Flue Gas HCl Concentrations to Theoretical Predictions for Parametric Tests at MoSES

Average Injection	Average M26	Average M26		
Rate,	Measurement of	Measurement of	Theoretical HCl	
pm equivalent in	Flue Gas Cl ₂ ,	Flue Gas HCl,	Concentration,	Measured/
dry coal	ppm, dry, $3\% O_2$	ppm, dry, 3% O ₂	ppm, dry, 3% O ₂	Theoretical, %
400	< 0.08	35.4	37	96
600	< 0.08	53.4	55	97
800	< 0.08	67.4	73	92

Table 11. Comparison of Measured Flue Gas HBr Concentrations to Theoretical Predictions for Parametric Tests at MoSES

Average Injection	Average M26	Average M26		
Rate,	Measurement of	Measurement of	Theoretical HBr	
ppm equivalent in	Flue Gas Br ₂ ,	Flue Gas HBr,	Concentration,	Measured/
dry coal	ppm, dry, $3\% O_2$	ppm, dry, 3% O ₂	ppm, dry, 3% O ₂	Theoretical, %
12.5	< 0.01	0.75	0.51	147
50	< 0.01	2.0	2.03	99
100	< 0.01	2.4	4.06	59
200	< 0.01	5.1	8.16	63

The measured SCEM data are shown in Figures 48 and 49 for the CaCl₂ and CaBr₂ tests, respectively. In general, each injection rate was maintained for at least 2 hours. Once the flue gas mercury concentrations steadied out, the injection rate was changed. For each injection rate, an average of the measured steady-state mercury concentrations was taken. Table 12 presents these average concentrations.

While Figure 49 presents all of the scrubber outlet mercury concentration data that were measured by the SCEM, only limited scrubber outlet data were used in the calculation of mercury removal for the parametric CaBr₂ tests. Significant problems were initially encountered while the gas was sampled at the scrubber outlet because the only available sampling ports were directly above the scrubber exit. As the mist-laden flue gas exited the scrubber and was sampled by the mercury extraction probe, large volumes of slurry would occasionally get pulled into the extraction probe (despite having a nozzle on the probe tip that was pointed in the opposite direction of flue gas flow). As the slurry was heated by the probe, the mercury in the slurry offgassed and was sampled by the SCEM, producing a positive bias in the scrubber outlet mercury concentrations. As the test program progressed, methods were devised to minimize this positive bias. These methods included 1) the use of a dual extraction loop, 2) decreasing the heating on the extraction probe to prevent spray-drying any captured slurry, and 3) daily preventive cleaning of the extraction probe. While these methods did not eliminate the problem, they reduced the occurrence of positively biased data at the FGD outlet. However, many of these techniques were not employed until the completion of the parametric test program.

The percentage of mercury present as oxidized mercury was calculated at the ESP inlet and ESP outlet locations. Table 13 shows these results. Figures 50 and 51 plot the mercury oxidation results for CaCl₂ and CaBr₂ injection, respectively.

For the first test days during parametric testing, the oxidation of mercury at the ESP inlet was significantly higher than at the ESP outlet. At the ESP inlet, the baseline oxidation was between 54% and 71%, while the ESP outlet oxidation was between 29% and 25%. The ESP inlet oxidation percentages were significantly higher than what was measured during all the other baseline measurement periods, when it was typically between 10% and 40%. The inertial gas separation (IGS) filter at the ESP inlet was replaced at the beginning of the fourth day of parametric testing; an increase in the elemental mercury concentration (and decrease in oxidation) measured at the ESP inlet was observed following IGS filter replacement; therefore, it is believed that the IGS filter was

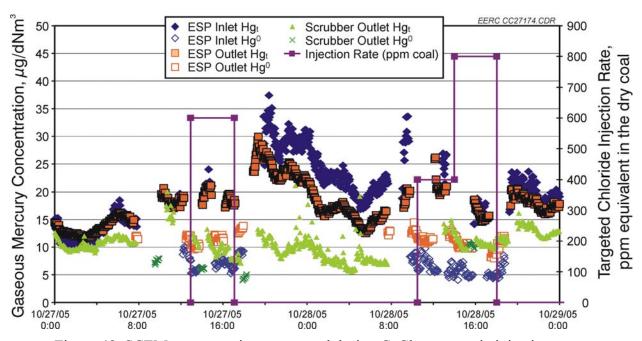


Figure 48. SCEM concentrations measured during CaCl₂ parametric injection tests.

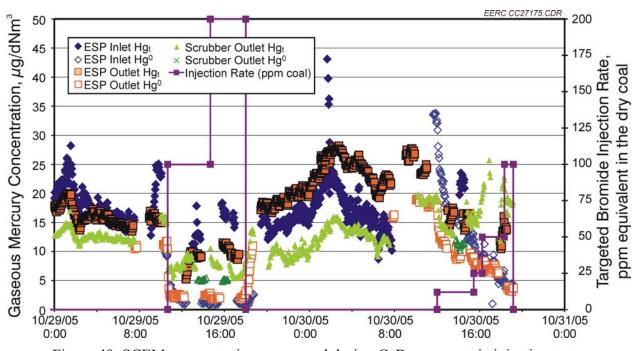


Figure 49. SCEM concentrations measured during CaBr₂ parametric injection tests.

Table 12. Average Mercury Concentrations During Parametric Injection Tests at MoSES

	Gas-Phase Mercury Concentrations,							
	$\mu g/dm^3$, 3% O_2							
	Targeted	ESP I	ESP Inlet ESP Outlet			Scrubber Outlet		
	Injection Rate,			Hg				
Chemical	ppm X in coal	Hg Total	Hg^0	Total	Hg^0	Hg Total	Hg^0	
Baseline	0	19.3	9.3	18.4	11.9	16.2	NA	
$CaCl_2$	600	21.1	6.8	19.6	11.0	10.2	6.2	
Baseline	0	28.2	7.9	19.3	12.7	NA^1	NA	
$CaCl_2$	400	25.0	7.0	21.0	11.6	13.6	NA	
$CaCl_2$	800	17.0	5.3	16.0	9.8	10.4	10.4	
Baseline	0	20.7	9.5	15.8	11.2	15.6	NA	
$CaBr_2$	100	12.0	1.3	8.7	2.4	8.1	5.1	
$CaBr_2$	200	16.1	1.1	10.1	2.2	6.3	5.1	
Baseline	0	NA	33.3	23.8	18.3	18.9	NA	
CaBr ₂	12	21.9	15.9	15.6	9.9	14.3	11.2	
CaBr ₂	25	NA	8.8	NA	7.1	16.9	NA	
CaBr ₂	50	NA	6.4	12.5	6.9	D^2	NA	
CaBr ₂	100	NA	4.2	NA	3.4	D	NA	

Not available because the value either was not measured or did not pass QC.

Table 13. Percent Oxidation of Mercury at ESP Inlet and Outlet Measured During Parametric Injection Tests

Measured During Farametric injection Tests				
		Targeted		
		Injection Rate,	Hg Oxidation	Hg Oxidation
Test Day	Chemical	ppm X in coal	at ESP Inlet*, %	at ESP Outlet*, %
1	Baseline	0	52	35
	$CaCl_2$	600	68	44
2	Baseline	0	72	34
	$CaCl_2$	400	72	45
	$CaCl_2$	800	69	39
3	Baseline	0	54	29
	$CaBr_2$	100	89	72
	CaBr ₂	200	93	78
4	Baseline	0	NA	23
	$CaBr_2$	12	27	37
	$CaBr_2$	25	60	50
	$CaBr_2$	50	71	45
	CaBr ₂	100	81	73

^{*} Total gas-phase mercury concentration was not available for these runs; therefore, percent oxidation was based on average total gas-phase mercury concentration measured during either the previous or following test.

² Deleted data because scrubber outlet probe received a slug of FGD slurry and caused increased measured mercury concentrations.

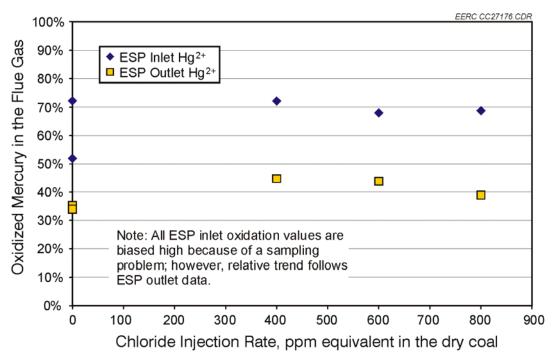


Figure 50. Percent oxidized mercury present at ESP inlet and outlet for CaCl₂ parametric injection tests.

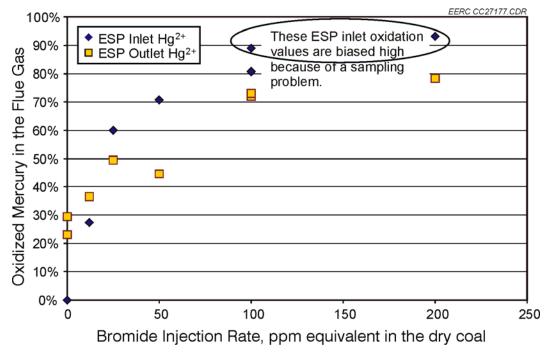


Figure 51. Percent oxidized mercury present at ESP inlet and outlet for CaBr₂ parametric injection tests.

oxidizing a portion of the mercury in the sampled flue gas. While the oxidation values at the ESP inlet are biased high for the first three test days of parametric testing, these values do show the same performance trends as the ESP outlet data for the two halogenated chemicals.

The parametric CaCl₂ tests showed only a nominal increase in mercury oxidation at the ESP inlet and ESP outlet locations. The gas-phase mercury at the ESP outlet reached a maximum of 45% oxidation at an injection rate of 400 ppm Cl equivalent in the dry coal as compared to a baseline oxidation of 35%. The oxidation of mercury at both the ESP inlet and ESP outlet locations did not increase with injection rates above 400 ppm Cl equivalent in the coal. In contrast, the injection of CaBr₂ resulted in up to 72% oxidation of the mercury at the ESP outlet at an injection rate of 100 ppm Br equivalent in the dry coal. The breaking point for the performance curve appears to be around 100 ppm Br equivalent in the coal. Increasing the injection rate to 200 ppm Br increased the oxidation from 72% up to only 78%.

Figures 52 and 53 show the percentage of mercury removal across the ESP and the FGD for the CaCl₂ and CaBr₂ injection tests, respectively. The baseline mercury removal across the ESP was approximately 20% during these test days, but was typically 0% during all other baseline periods in the test program. Neither the CaCl₂ nor the CaBr₂ resulted in an increase in mercury removal across the ESP.

The mercury removal across the FGD increased from 12% at baseline to approximately 45% during the CaCl₂ injection tests. These results agree well with the measured 45% oxidation of mercury at the FGD inlet (ESP outlet). Because of sampling problems (described above) at the FGD outlet during the CaBr₂ parametric test days, virtually none of the FGD outlet data were usable. Therefore, no conclusions can be drawn from the parametric tests about the effect of CaBr₂ on mercury removal by the FGD scrubber. However, the effect of CaBr₂ on mercury removal across the FGD is well documented in the long-term testing.

Because of the sampling problems at the FGD outlet during the CaBr₂ injection tests, it was not possible to compare the effect of halogen identity on net flue gas mercury removal across the ESP/FGD system. The parametric tests for the CaCl₂ showed that CaCl₂ did not achieve the oxidation needed to meet the mercury removal target of 55% for the project. On the other hand, CaBr₂ was shown capable of achieving high mercury oxidation that might be sufficient to achieve the mercury removal goals for the project; therefore, CaBr₂ was selected for the long-term tests. For the first 2-week continuous injection test, an injection rate of 50 ppm Br equivalent in the coal was selected. Based on the parametric oxidation results, this injection rate appeared capable of achieving the mercury removal target of 55%.

4.3.2.3 Long-Term Test Results

Two longer-term, continuous injection tests were executed as part of this test program. In the first 2-week continuous test, CaBr₂ was injected at a target injection rate of 50 ppm Br equivalent in the dry coal. In the second 2-week test, CaBr₂ was injected at a target injection rate of 100 ppm Br equivalent in the coal. At the end of the second 2-week test, the injection rate was further increased in an attempt to achieve higher mercury oxidation and removal rates.

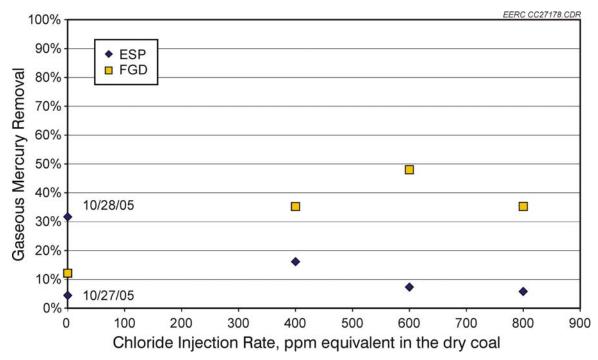


Figure 52. Mercury removal across the ESP and FGD for CaCl₂ during parametric injection tests at MoSES.

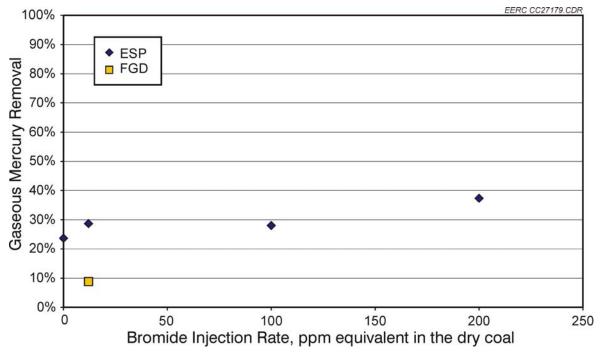


Figure 53. Mercury removal across the ESP and FGD for CaBr₂ during parametric injection tests at MoSES.

4.3.2.4 Evaluation of Actual CaBr₂ Injection Rates

During the $CaBr_2$ injection tests, the approximate targeted injection rate was maintained by monitoring the coal feed rate and the solution pump rate and by using measurements of the solution density to estimate the bromide solution content. The pumped $CaBr_2$ solution was collected daily during the test program. At the conclusion of the long-term tests, these solution samples were analyzed in URS Austin's laboratory with ion chromatography for the true bromide content. The true bromide content was used in conjunction with the solution density and coal feed rate (from plant data) to calculate the actual injection rates maintained during the test program. In addition, flue gas halogen concentrations were monitored daily at the ESP inlet using Method 26.

Overall, the calculated injection rates, presented in Figure 54, were slightly higher than the target injection rate of 50 ppm Br equivalent in the dry coal for the first 2-week test period. Over the course of the 2-week test period, the actual injection rate was an average 55 ppm Br equivalent in the coal. Because of fluctuations in the CaBr₂ pump response to the changing load and pulverizer speeds, the injection rate temporarily reached as low as 45 ppm and as high as 90 ppm over the course of the test period.

Figure 54 also shows the results of daily Method 26 monitoring of flue gas bromide concentrations were made daily during the test period (complete results are tabulated in Appendix C). During baseline (no CaBr₂ injection), the flue gas HBr content was less than 0.05 ppm (dry, 3% O₂). The HBr concentration of the flue gas averaged 1.8 ppm (dry, 3% O₂) over the course of the first 2-week injection test period. Because of the fluctuations in the feed rate, the HBr concentration went as high as 2.5 and as low as 1.4 ppm.

Although the target injection rate for the second 2-week test period was initially 100 ppm Br equivalent in the coal. The injection rate was increased toward the end of the test period in an attempt to realize higher oxidation and removal rates of mercury. The actual injection rate is shown in Figure 55. Over the course of the 2-week test period (December 2–12, 2005), the actual injection rate averaged 113 ppm Br equivalent in the coal. The injection rate ranged from as low as 97 ppm to as high as 158 ppm. On December 12, the injection rate was increased to approximately 200 ppm Br, and on December 13, the injection rate was further increased to an injection rate of 330 ppm Br equivalent in the coal.

Results of daily Method 26 measurements of flue gas bromide/bromine concentrations are also shown in Figure 55 (results for individual runs are tabulated in Appendix C). The Br₂ concentration of the flue gas was less than the detection limit of 0.02 ppm during all the long-term test periods. During baseline (no CaBr₂ injection), the flue gas HBr content was less than 0.06 ppm (dry, corrected to 3% O₂) toward the end of the test period. The HBr concentration of the flue gas averaged 3.25 ppm (dry, 3% O₂) during the period when the average injection rate was 113 ppm Br equivalent in the coal (Table 14). When the injection rate was increased to 193 ppm Br equivalent in the coal, the flue gas HBr concentration increased to 5.6 ppm; when the injection rate was further increased to 330 ppm Br equivalent in the coal, the flue gas HBr concentration increased to 8.1 ppm.

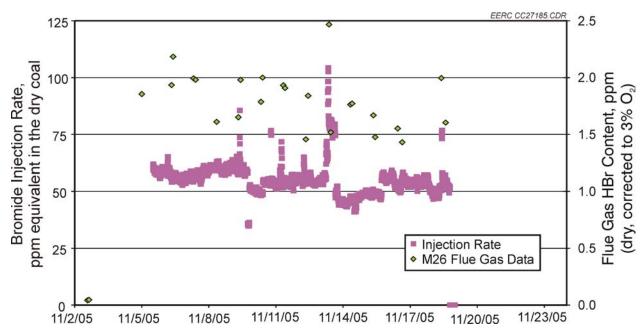


Figure 54. Actual additive injection rate of CaBr₂ and M26 measurements during first 2-week long-term test period at MoSES.

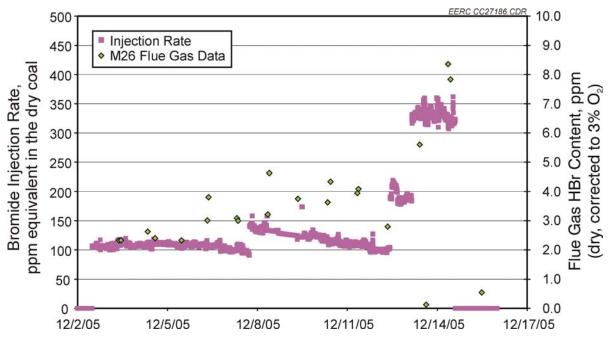


Figure 55. Actual additive injection rate of CaBr₂ and M26 measurements during first 2-week long-term test period at MoSES.

Table 14. Comparison of Measured Flue Gas HBr Concentrations to Theoretical Predictions for MoSES Long-Term Tests

	Average M26	Average M26		
Average Injection	Measurement of	Measurement of	Theoretical HBr	Measured/
Rate, ppm Br	Flue Gas Br ₂ ,	Flue Gas HBr,	Concentration,	Theoretical,
equivalent in dry coal	ppm, dry, $3\% O_2$	ppm, dry, 3% O ₂	ppm, dry, 3% O ₂	%
55	< 0.02	1.8	2.2	82
113	< 0.02	3.25	4.6	71
193	< 0.02	5.6	7.8	72
330	< 0.02	8.1	13.4	60

The theoretical flue gas HBr concentration was computed from the actual $CaBr_2$ injection rate and the flue gas flow rate. The flue gas flow rate was estimated from an EPA Method 19 F-factor calculation. For the theoretical calculation, it was assumed that all of the injected bromide converts to flue gas HBr. Table 14 compares the average Method 26 measurement of flue gas HBr content to the theoretical prediction. The measured flue gas HBr concentration correlated relatively well with theoretical predictions. At the lowest injection rate, the measured concentration was 82% of the theoretical concentration. As the injection rate increases, the measured concentration decreased to only 60% of the theoretical concentration.

While most flue gas halogen monitoring was carried out nonisokinetically with the Method 26 mini-impinger method, one set of Method 26A samples was collected during 1 day of the injection test at 55 ppm Br equivalent in the coal. An isokinetic, full-traverse Method 26A was conducted at the ESP inlet and an isokinetic, single-point Method 26A was conducted at the scrubber outlet locations. The results are summarized in Table 15. At the ESP inlet, the flue gas chlorine and bromine concentrations were below the detection limit of the method. The flue gas HBr concentration was 1.85 ppm HBr (dry, 3% O₂), which matched the average flue gas HBr concentration measured with the nonisokinetic Method 26. The flue gas HCl concentration measured by Method 26A was 1.5 ppm HCl, which was within the range of HCl concentrations measured with Method 26.

The Method 26A data at the scrubber outlet were problematic. The scrubber outlet Method 26A measurements were made in the same row of ports that the Ontario Hydro and SCEM measurements were made. As already discussed in regard to the SCEM measurements, these ports were located directly above the scrubber exit, and FGD slurry was frequently accidentally pulled into the sample probes. Therefore, scrubber slurry contaminated the sample train at the FGD outlet, biasing the results high.

Both HCl and HBr should be scrubbed with nearly 100% efficiency by the FGD scrubber. Therefore, the expected scrubber outlet HCl and HBr concentrations should be close to zero. However, these Method 26A measurements indicated an average of 15.8 ppm HCl at the scrubber outlet, which is ten times higher than the inlet HCl concentration. The average Method 26A HBr concentration at the scrubber outlet was 0.9 ppm HBr, which indicated that only 50% of the HBr was scrubbed. These Method 26A measurements are unrealistic; therefore, the results have been voided and are not reported in Table 15.

Table 15. Method 26A Measurement Results from the MoSES Long-Term Injection Test at 55 ppm Br Equivalent in the Coal (all results expressed as ppm, dry, 3% O₂)

	Location/						
Condition	Run No.	Date	Start Time	Cl_2	HC1	Br_2	HBr
55 ppm Br	ESP Inlet 1	11/16/05	8:32	< 0.02	1.56	< 0.004	1.84
55 ppm Br	ESP Inlet 2	11/16/05	10:30	< 0.02	1.4	< 0.004	1.87
55 ppm Br	ESP Inlet 3	11/16/05	12:25	< 0.03	1.46	< 0.004	1.86
	ESP Inlet		AVERAGE	< 0.02	1.49	< 0.004	1.86

4.3.2.5 Summary of Mercury Data from Long-Term Injection Test No. 1

Figure 56 shows the SCEM total mercury concentrations measured at the ESP inlet, ESP outlet, and FGD outlet over the course of the first 2-week continuous injection test. Figures 57 through 59 show hourly averages of the total and elemental mercury concentrations measured at each of the three locations.

Prior to the start of the injection test, the scrubber outlet total mercury concentration ranged from 10 to 20 $\mu g/dNm^3$ (3% O_2). During the first day of the injection test, the ESP inlet and ESP outlet elemental concentrations decreased significantly, and the scrubber outlet mercury concentration decreased to 3–7 $\mu g/Nm^3$. On the following 6 days, the scrubber outlet mercury concentration steadily increased to approximately 12 $\mu g/Nm^3$; however, the ESP inlet concentration also increased during this time period. On November 11, 2005, the scrubber C module (which is the module on which SCEM measurements were being made) was taken out of service for 2 days. The scrubber C module was placed back in service on November 13. During the 2 days back in service, the scrubber outlet mercury concentration steadily increased from 5 to 12 $\mu g/Nm^3$. For the remainder of the test period (November 15 to 18), the scrubber outlet mercury concentrations remained in this range.

Over the course of testing with the 55-ppm-Br-equivalent injection rate, the percent of oxidized mercury at the ESP inlet and outlet locations ranged as high as 80% to as low as 10% (as illustrated in Figure 60). The data for the test period indicate that, on average, the ESP inlet mercury was 60% oxidized and the ESP outlet mercury was 58% oxidized. Despite the favorable mercury speciation at the inlet to the FGD, the average mercury removal measured across the FGD scrubber was only 18%.

Figure 61 shows the removal of mercury across the ESP, FGD, and ESP/FGD systems. The mercury removal across the ESP averaged 18%, indicating perhaps some mercury removal across the ESP (analytical uncertainty of the SCEMs is typically quoted as ±20%). The average mercury removal across the ESP/FGD system was 44% over the injection test period. From the start of the injection test on November 5–13, 2005, the removal of mercury across the FGD and ESP/FGD system typically ranged from 50% to 80% (with some short periods indicating as low as 25% removal). After November 13 (when the scrubber C module was placed back into service), the removal of mercury across the scrubber started to decline, until the scrubber outlet

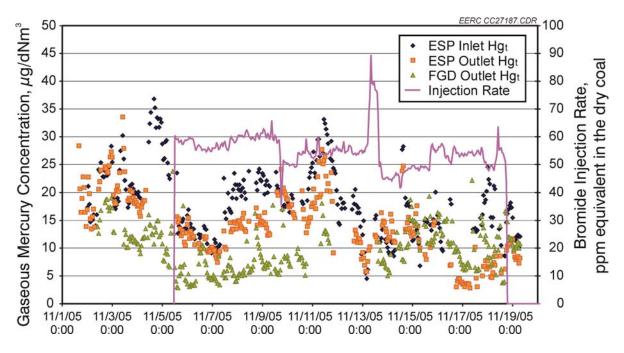


Figure 56. Hourly averaged total mercury concentration from SCEM data collected during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

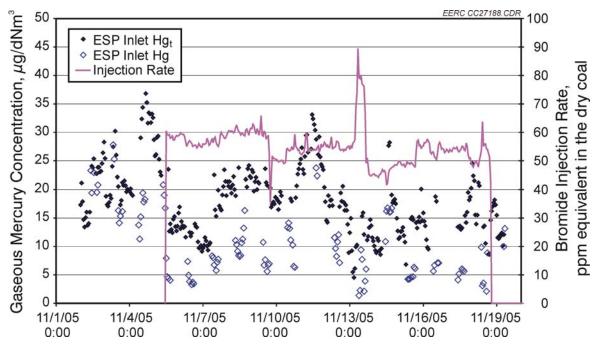


Figure 57. ESP Inlet total and elemental mercury concentrations measured during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

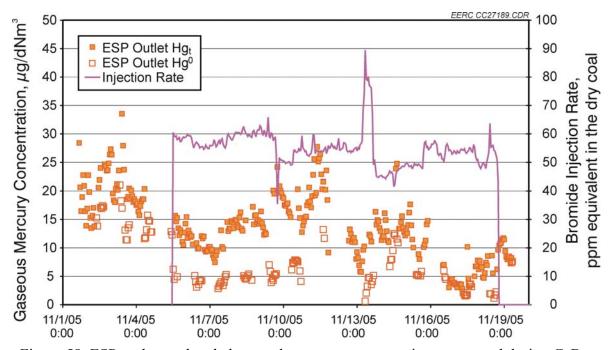


Figure 58. ESP outlet total and elemental mercury concentrations measured during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

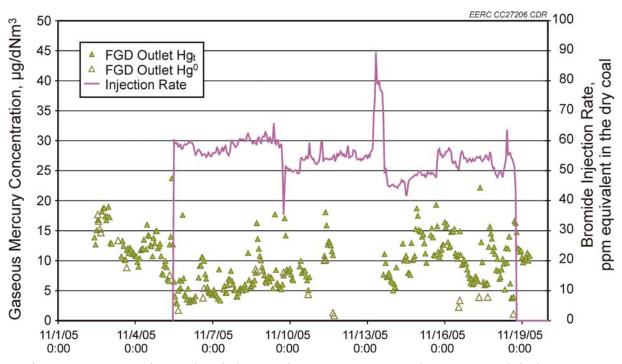


Figure 59. FGD outlet total and elemental mercury concentrations measured during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

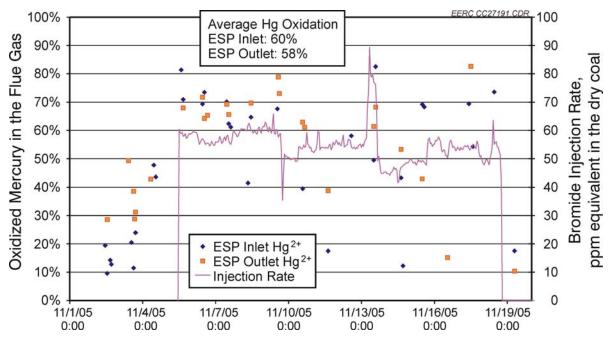


Figure 60. Percent oxidized mercury at the ESP inlet and outlet during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

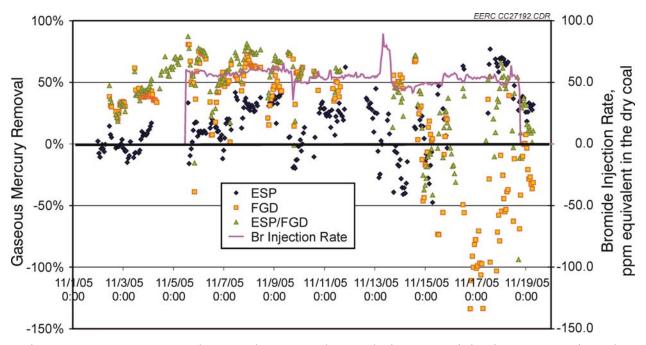


Figure 61. Mercury removal across the ESP and FGD during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

mercury concentration was higher than the inlet concentration. One possibility for this phenomenon could be a positive bias in the scrubber outlet extraction system, caused by the vaporization of mercury in the FGD slurry accidentally captured in the extraction loop. However, the scrubber outlet extraction loop was kept under constant supervision, cleaning, and maintenance during this test program. Typically, when the scrubber outlet mercury concentrations were biased high, the biased period lasted for a finite period of time on the order of a few to several hours. In this case, the elevated scrubber concentrations were maintained for several days, despite cleaning of the scrubber extraction loop.

Figure 62 compares the scrubber outlet total mercury concentration to the scrubber inlet (ESP outlet) elemental mercury concentration. In a situation with no mercury reemissions across the scrubber, these two values should be equal. Figure 62 shows that the values are equivalent for the baseline period prior to the injection test and for the first half of the injection test (through November 14, 2005). After that period, the scrubber outlet total mercury concentration was, at times, more than double the scrubber inlet elemental mercury concentration.

Based on a preliminary evaluation of these data made immediately following the conclusion of the first 2-week injection test, the project team elected to conduct the second 2-week injection test at double the CaBr₂ injection rate. The results for the second 2-week injection test are presented in the next subsection.

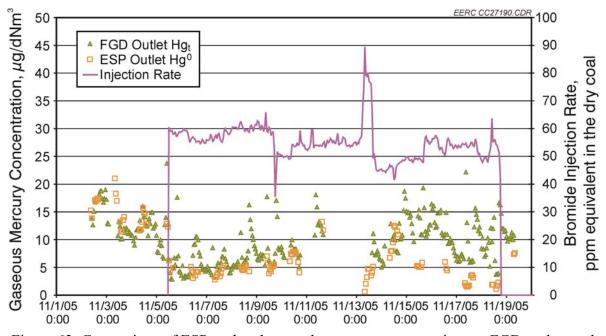


Figure 62. Comparison of ESP outlet elemental mercury concentrations to FGD outlet total mercury concentrations during CaBr₂ injection at approximately 55 ppm Br equivalent in the dry coal, first 2-week long-term test at MoSES.

4.3.2.6 Summary of Mercury Data from Long-Term Injection Test No. 2

The second long-term mercury control test involved CaBr₂ injection at a nominal 100 ppm Br equivalent in dry coal. Figure 63 shows the hourly averages of the SCEM total mercury concentrations measured at the ESP inlet, ESP outlet, and FGD outlet over the course of the second 2-week continuous injection test. Figures 64 through 66 show the total and elemental mercury concentrations measured at each of the three locations.

Prior to the start of the injection test, the scrubber outlet total mercury concentration ranged from 12 to 19 $\mu g/dNm^3$ (3% O₂). During the first day of the injection test, the ESP inlet and ESP outlet elemental concentrations decreased significantly, and the scrubber outlet mercury concentration decreased to 4 $\mu g/Nm^3$. During the next 10 days of the injection test, in which the injection rate averaged 113 ppm Br equivalent in the coal, the scrubber outlet mercury concentration ranged from 0.5 to 11 $\mu g/Nm^3$. However, the scrubber outlet mercury concentration was typically less than 5 $\mu g/Nm^3$; only during short periods of a few hours did the scrubber outlet mercury concentration exceed 5 $\mu g/Nm^3$. A 1-day test showed that increasing the injection rate to 193 ppm Br equivalent in the coal resulted in the scrubber outlet concentration being maintained below 4 $\mu g/Nm^3$. The injection rate was increased to 330 ppm Br equivalent in the coal, and the scrubber outlet mercury concentration was maintained below 3 $\mu g/Nm^3$ for the 2-day duration of this injection rate.

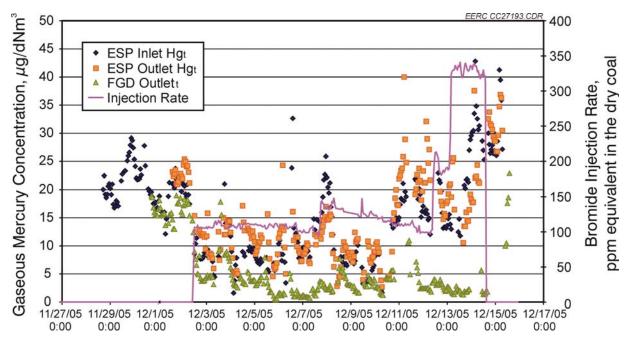


Figure 63. Hourly averaged SCEM data collected during the second long-term CaBr₂ injection test at MoSES.

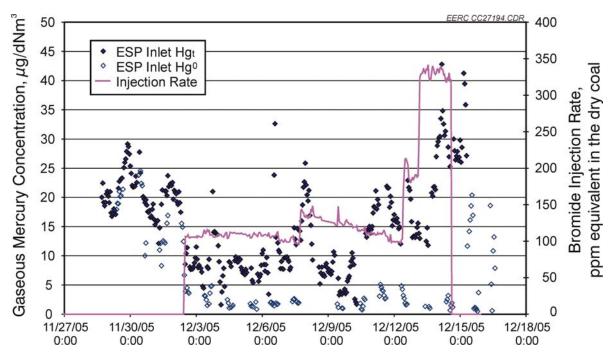


Figure 64. ESP inlet total and elemental mercury concentrations measured during the second long-term CaBr₂ injection test at MoSES.

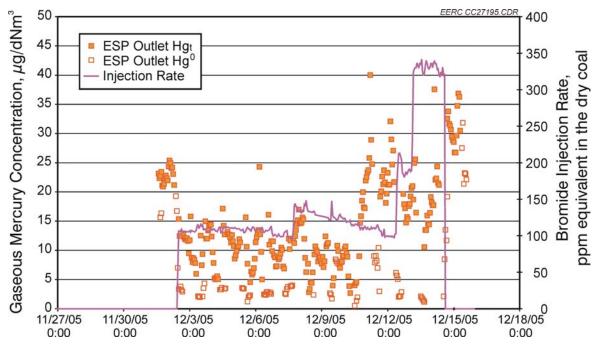


Figure 65. ESP outlet total and elemental mercury concentrations measured during the second long-term CaBr₂ injection test at MoSES.

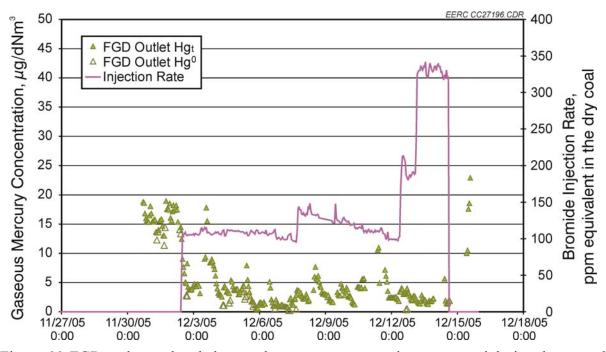


Figure 66. FGD outlet total and elemental mercury concentrations measured during the second long-term CaBr₂ injection test at MoSES.

Figure 67 shows the calculated percent oxidation of mercury at the ESP inlet and outlet locations over the course of the test. The average oxidation of mercury during each tested injection rate in the second long-term test period is shown in Table 16. At an injection rate of 113 ppm Br equivalent in the coal, the oxidation of mercury at the ESP inlet was an average 80%. The oxidation of mercury at the ESP outlet was lower but similar at 70%. Increasing the injection rate to 193 ppm Br equivalent in the coal increased the oxidation of mercury at the ESP inlet and outlet to 93% and 88%, respectively. Further increasing the CaBr₂ injection rate to 330 ppm in the coal did not result in further increases in the oxidation of mercury.

The oxidation of mercury at the FGD outlet is also shown in Table 16. In general, one would expect the mercury exiting the FGD to be present almost entirely as elemental mercury. During the baseline period prior to this second long-term injection test and through the first few days of the injection test, the oxidation of mercury at the FGD outlet was very low. However, as the test progressed, the oxidation of mercury at the FGD outlet increased. It is assumed that this was a sampling artifact, as the FGD scrubber outlet extraction system was very difficult to maintain (however, no signs of corrosion were seen in the IGS filter).

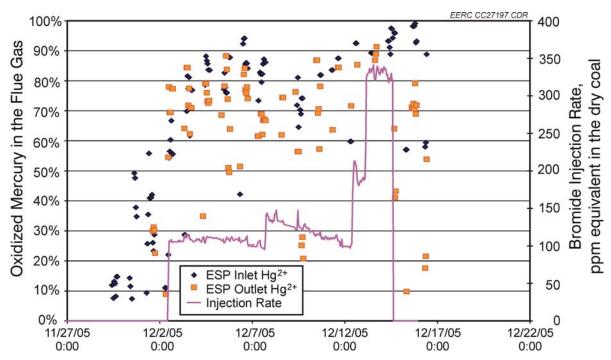


Figure 67. Percent oxidized mercury at the ESP inlet and outlet during the second long-term CaBr₂ injection test at MoSES.

Table 16. Ratio of Oxidized Mercury to Total Mercury Content of the Flue Gas at the ESP Inlet and ESP Outlet During Second Long-Term Injection Test at MoSES

CaBr ₂ Injection Rate,			
ppm, dry, $3\% O_2$	ESP Inlet	ESP Outlet	FGD Outlet
113	80%	70%	59%
193	93%	88%	88%
330	93%	89%	NA

Figure 68 and Table 17 show the removal of mercury across the ESP, FGD, and ESP/FGD systems. The average mercury removal across the ESP ranged from –24% to +28% for the injection rates tested. These values are slightly greater than the uncertainty of ±20% assigned to the SCEM measurement method. Therefore, from these data, there does not appear to be significant removal of mercury across the ESP during CaBr₂ injection, except perhaps at the highest injection rate of 330 ppm Br equivalent in the coal. The average mercury removal across the ESP/FGD system was 59% at an average injection rate of 113 ppm Br equivalent in the coal. At an injection rate of 193 ppm Br equivalent in the coal, the mercury removal across the ESP/FGD system increased to 83%. The average mercury removal increased still further to 89% at an injection rate of 330 ppm Br equivalent in the coal. However, it should be noted that the tests at 193 and 330 ppm Br lasted for, at most, 2 days each; while the test at 113 ppm Br equivalent in the coal lasted for 10 days. Thus longer-term testing is needed to verify the results of these 1- and 2-day high-injection-rate tests.

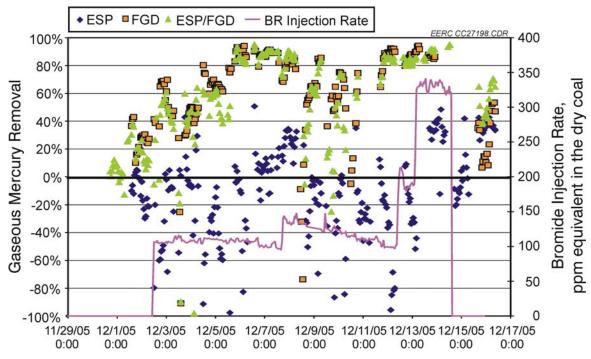


Figure 68. Mercury removal across the ESP and FGD during the second long-term CaBr₂ injection test at MoSES.

Table 17. Average Mercury Removal Across the ESP and FGD During the Second Long-Term Injection Test at MoSES

Term injection rest at	MUSES		
CaBr ₂ Injection Rate,			Mercury Removal
ppm, dry, 3% O ₂	Across ESP	Across FGD	across ESP/FGD
113	-24%	64%	59%
193	-17%	85%	83%
330	28%	89%	90%

Figure 69 compares the scrubber outlet total mercury concentration to the scrubber inlet (ESP outlet) elemental mercury concentration. The values are nearly equivalent for the entire test period.

4.3.2.7 Effect of Plant Operating Parameters on Gas-Phase Mercury Concentrations

The ESP inlet total gas-phase mercury concentration was plotted along with the following three unit operating parameters: unit load, air heater outlet temperature, and SO₂ concentration entering the scrubber. Figures 70 through 72 are the plots for the first 2-week injection test. Figures 73 through 75 are the plots for the second 2-week injection test.

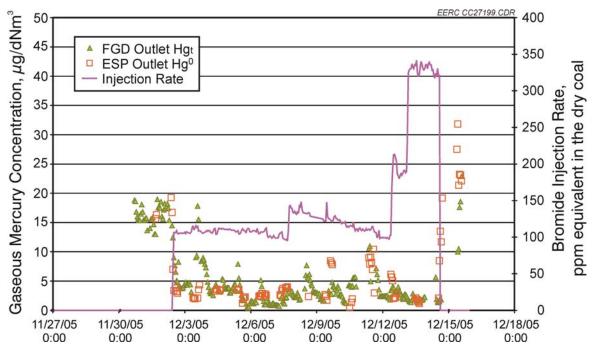


Figure 69. Comparison of ESP outlet elemental mercury concentrations to scrubber outlet total mercury concentrations during the second long-term CaBr₂ injection test at MoSES.

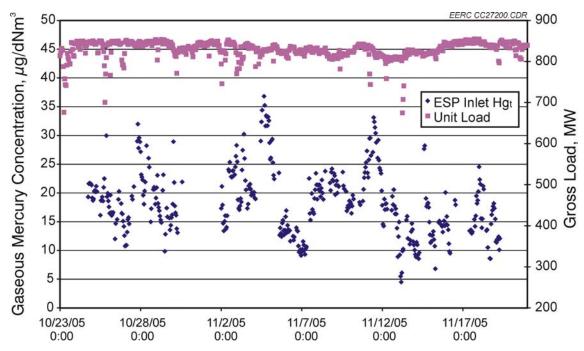


Figure 70. Unit load during the first 2-week CaBr₂ injection test period at MoSES.

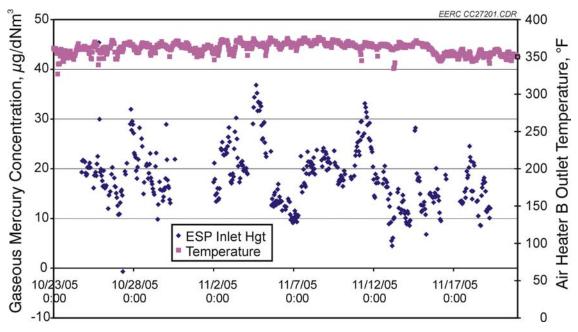


Figure 71. Air heater outlet temperature during the first 2-week CaBr₂ injection test at MoSES.

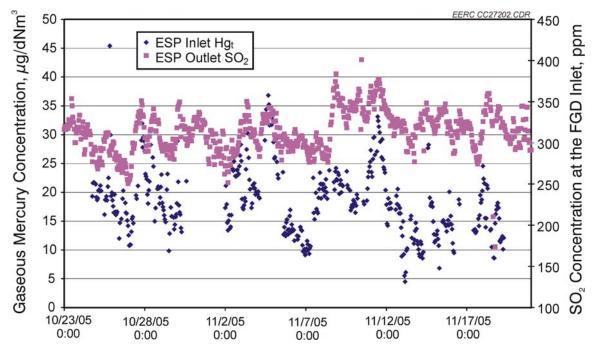


Figure 72. FGD inlet SO₂ concentration during the first 2-week CaBr₂ injection test at MoSES.

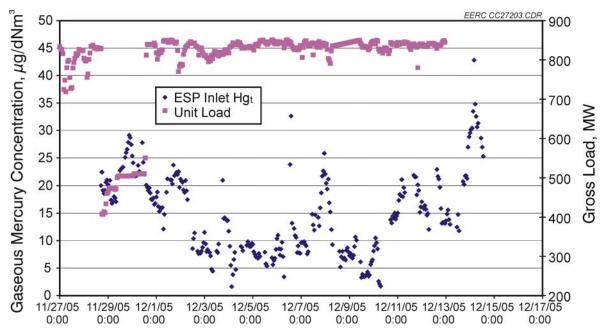


Figure 73. Unit load during the second 2-week CaBr₂ injection test period at MoSES.

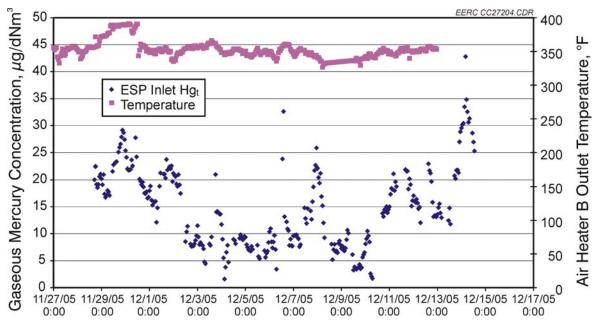


Figure 74. Air heater outlet temperature during the second 2-week CaBr₂ injection test period at MoSES.

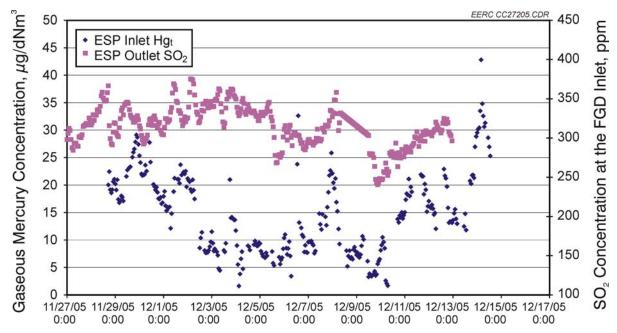


Figure 75. FGD inlet SO₂ concentration during the second 2-week CaBr₂ injection test period at MoSES.

The unit load was very constant throughout both sets of long-term injection tests, ranging from 790 to 850 MW, with only one short exception at the beginning of the long-term test. This was the period of November 28–30, in which the scrubber C module was out of operation, and the unit load was decreased to 500 MW.

The air heater outlet temperature went through regular daily swings between 175° and 190°C (350° and 375°F) during the first 2-week injection test. During the period of reduced load prior to the second long-term test, the air heater outlet temperature was atypically high at 200°C (390°F). Once the unit load was restored, the air heater outlet temperature ranged between 170° and 180°C (335° and 360°F) for the second 2-week injection test. This temperature range is lower than during the first injection test; furthermore, the regularity of daily swings between a maximum and minimum temperature was not pronounced.

The SO₂ concentration of the flue gas entering the FGD scrubber tower C generally correlated with the ESP inlet total mercury concentration. The SO₂ concentration ranged over a fairly narrow range between 240 and 375 ppm; however, a cursory inspection of Figures 72 and 75 indicate that inlet total mercury concentrations increased when flue gas SO₂ concentrations increased. This result is expected, as high-sulfur coal tends to have high mercury concentrations. Coal samples were gathered daily during the test program and have been analyzed for a variety of parameters, including mercury and sulfur content. The results of these coal analyses have not yet been evaluated.

5.0 CONCLUSIONS AND PLANNED ACTIVITIES FOR NEXT QUARTER

5.1 Task 1 – MRY Testing

5.1.1 Overall Conclusions

- The parametric testing was nearly completed during the January March quarter. The preliminary results of the initial parametric testing indicated that SEA1 did not show the level of oxidation necessary to achieve the 55% level of control. SEA2 showed much higher removal rates than SEA1. The addition of small amounts of carbon enhanced the removal of mercury across the ESP and FGD. The removal is taking place in the ESP and not in the FGD.
- Longer-term testing (1 to 2 months) of chemical addition was conducted to enhance Hg oxidation and capture in the ESP and wet FGD at the MRY plant. Initial testing of SEA2 injection alone at injection rates of 60–100 ppm was conducted. Removal rates of mercury were found to be as high as 75%, but only at SEA2 injection rates greater than 100 ppm. The quantity of SEA2 required was above the level anticipated based on pilot-scale studies. The effectiveness of the SEA2 may have been diminished because of the high sodium and calcium contents of the lignite fired.
- Longer-term testing was continued by injecting SEA2 at about 60 ppm along with a small quantity (0.15 lb/Macf) of PAC which was required to meet the target of 55% mercury removal. Injection of SEA2, in combination with a nominal 0.15-lb/Macf PAC injection, was initiated on April 19 and continued until May 18, 2005, when the supply of SEA2 was exhausted. PAC injection continued for several hours on May 19 after the SEA2 ran out in order to empty the PAC Super Sack feeding the PortaPac injection system. During the SEA2 PAC injection, the 55% mercury removal target was exceeded 25% of the time, with removal rates as high as 65%; 50% of the time, the removal rate was between 50% and 55%.

5.1.2 Conclusions for This Quarter

• Corrosion probes were analyzed, and the results indicated that the economizer and AHI long-term test coupons have more rough or cracking metal surfaces, possibly indicating more corrosion as a result of being exposed to the SEA2 additive. The deposit layers of ECM, AHI, and AHO long-term coupons have more or less higher S, Ca, Na, and K concentrations, indicating possible alteration of deposit chemistry caused by exposure to SEA2. In summary, the SEA2 addition may have caused more corrosion of the ECM and AHI long-term coupons. Longer tests and further investigation are necessary to confirm the effect of SEA2 on steel corrosion. The increase in corrosion may also be due to changes in coal quality between baseline and long-term testing. Analysis of the coal properties will be conducted next quarter to determine if coal properties contributed to the changes in deposition behavior and corrosion potential.

5.1.3 Planned Activities

• Sample analysis and data interpretation for MRY will be completed next quarter.

5.2 Task 2 – Monticello Testing

5.2.1 Conclusions for This Quarter

Full-scale tests were performed at Monticello Unit 3 (fall 2005) to evaluate the effectiveness of chemical addition on Hg control across an ESP wet scrubber configuration.

- Two longer-term, continuous injection tests were executed as part of this test program. In the first 2-week continuous test, CaBr₂ was injected at a target injection rate of 50 ppm Br equivalent in the dry coal. In the second 2-week test, CaBr₂ was injected at a target injection rate of 100 ppm Br equivalent in the coal. At the end of the second 2-week test, the injection rate was further increased in an attempt to achieve higher mercury oxidation and removal rates.
- During long-term (2-week) Br injection at a target injection rate of 50 ppm Br equivalent in the dry coal, the mercury removal across the ESP averaged 18%, indicating perhaps some mercury removal across the ESP (analytical uncertainty of the SCEMs is typically quoted as ±20%). The average mercury removal across the ESP/FGD system was 44% over the injection test period.
- During long-term (2-week) Br injection at a target injection rate of 100 ppm Br equivalent in the dry coal, the average mercury removal across the ESP ranged from –24% to +28% for the injection rates tested. These values are slightly greater the uncertainty of ±20% assigned to the SCEM measurement method. Therefore, from these data, there does not appear to be significant removal of mercury across the ESP during CaBr₂ injection, except perhaps at the highest injection rate of 330 ppm Br in the coal.
- The average mercury removal across the ESP/FGD system was 59% at an average injection rate of 113 ppm Br in the coal.

At an injection rate of 193 ppm Br in the coal, the mercury removal across the ESP/FGD system increased to 83%. The average mercury removal increased still further to 89% at an injection rate of 330 ppm Br in the coal.

5.2.2 Planned Activities

Analysis of data collected from the long-term chemical injection tests at MoSES will
continue. The coal, ash, and FGD samples were analyzed in this quarter for a number of
parameters. The results of these analyses will be evaluated in the next quarter. The mercury
oxidation and removal results will be further explored with respect to unit operating
parameters. An economic analysis will be conducted with the data gathered from the longterm injection tests.

6.0 REFERENCES

- 1. Clean Air Act Amendments of 1990. U.S. Public Law 101-549, 1990; *Code of Federal Regulations*, Section 302, Title 42, 1990.
- 2. U.S. Environmental Protection Agency. *Mercury Study Report to Congress*; EPA-452/R-97-003; EPA Office of Air Quality Planning and Standards, U.S. Government Printing Office: Washington, DC, Dec 1997.
- 3. U.S. Environmental Protection Agency. A Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units: Final Report to Congress; EPA-453/R-98-004a; EPA Office of Air Quality Planning and Standards, U.S. Government Printing Office: Washington, DC, Feb 1998.
- 4. U.S. Environmental Protection Agency. *Information Collection Request*; 1999.
- 5. Pavlish, J.H.; Holmes, M.J. Mercury Control for Lignite-Fired Power Plants Poses a Challenge. *Center for Air Toxic Metals Newsletter* **2002**, *8* (1), 6.
- 6. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Process. Technol.* **2003**, *82* (2, 3), 89–165.
- 7. Sjostrom, S.; Richardson, C.; Chang, R. *Evaluation of Mercury Emissions and Control Options for Great River Energy*; Final Report for North Dakota Industrial Commission; June 2001.
- 8. Chang, R.; Strohfus, M. *The Evaluation of Chemical Additives for Mercury Emission Control at Great River Energy*; Final Report for the North Dakota Industrial Commission; Jan 2003.
- 9. Thompson, J.S.; Holmes, M.J.; Laudal, D.L. *Long-Term Monitoring at North Dakota Power Plants*; Final Report for the North Dakota Industrial Commission; March 2003.
- 10. Laudal, D.L.; Pavlish, J.P.; Graves, J.; Stockdil, D. Mercury Mass Balances: A Case Study of Two North Dakota Power Plants. In *Proceedings of the AWMA Mercury in the Environment Specialty Conference*; AWMA VIP91, 1999; pp 340–34.
- Benson, S.A.; Crocker, C.R.; Galbreath, K.C.; Gunderson, J.R.; Holmes, M.J.; Laumb, J.D.; Mackenzie, J.M.; Olderbak, M.R.; Pavlish, J.H.; Yan, L.; Zhuang, Y. Final Report: *Pilot-and Full-Scale Demonstration of Advanced Mercury Control Technologies for Lignite-Fired Power Plants*; U.S. Department of Energy Cooperative Agreement No. DE-FC26-03NT41897.

APPENDIX A

SAMPLE DATES AND TIMES FOR FLUE GAS SAMPLES AND PROCESS SAMPLES AT MONTICELLO SES UNIT 3

APPENDIX B

SCEM DATA ANALYSIS METHODOLOGY FOR MONTICELLO SES UNIT 3

SCEM DATA ANALYSIS METHODOLOGY FOR MONTICELLO SES UNIT 3

The mercury semicontinuous emission monitors (SCEMs) use a gold amalgamation column coupled with a cold-vapor atomic absorption (CVAA). The flue gas is conditioned to remove the acid gas constituents (which can harm the gold's ability to adsorb mercury). It is also conditioned either to convert all the mercury to the elemental phase or to remove the oxidized mercury, leaving just the elemental phase. The CVAA can only detect the elemental form of mercury.

A measured flow rate of conditioned flue gas is passed over the gold amalgamation column for a fixed period of time. The flow rate is measured by a mass flowmeter. The flowmeter is calibrated to generate flow rates in the units of normal cubic meters (Nm³), where normal means the gas flow has been corrected to 32°F (0°C).

As the flue gas passes over the gold, the mercury in the flue gas adsorbs to the gold. Once a measured quantity of flue gas has passed over the gold, the gold is heated to desorb the mercury. This desorbed mercury is detected by the CVAA. The size of the peak generated by the CVAA correlates to a mass of mercury, as determined by a calibration curve. To produce the mercury concentration in $\mu g/Nm^3$, the mass of mercury is divided by the volume of flue gas sampled.

These mercury measurements are initially calculated at the actual O_2 concentration in the duct. For each mercury concentration, an oxygen concentration is measured. The mercury data are corrected to a 3% O_2 basis in order to account for dilution effects from location to location. The calculation for conversion to 3% O_2 is:

Hg [
$$\mu$$
g/Nm³ at 3% O₂] = Hg [μ g/Nm³ at x% O₂] × (20.9-3) / (20.9-x)

where x represents the actual O₂ concentration measured.

Each mercury SCEM produces a datum point every 3 to 7 minutes, depending on the sample time needed to collect a detectable amount of mercury on the gold. The sample time increases as the flue gas mercury concentration decreases.

Methodology for Data Analysis of Parametric Results

A parametric test condition consists of an oxidation enhancement agent type and an injection rate. Mercury SCEMs were employed at the electrostatic precipitator (ESP) inlet, ESP outlet, and flue gas desulfurization (FGD) outlet locations. An average mercury concentration was calculated for each location at each test condition. Each test condition typically lasted from 2 to 3 hours. During each test period, flue gas mercury concentrations were measured by the SCEMs. The test period was run long enough for the mercury concentrations to reach a steady-state. At each location the steady state data were averaged to generate an average mercury concentration for the test condition. Mercury removals across the ESP, FGD, and ESP/FGD system were calculated for each injection rate using these average mercury concentrations.

Methodology for Data Analysis of Long-Term Results

The long-term halogen injection test was run for two 2-week periods. Over this time period, mercury SCEM data were collected every 3 to 7 minutes at the ESP inlet, ESP outlet, and FGD outlet locations. Because of the huge volume of data, the mercury concentrations were reduced to 1-hour averages. These 1-hour averages were used for the plots in this report, and for calculations of percent removal across the ESP and FGD.

APPENDIX C METHOD 26 RESULTS

					All values in a	opmv, dry, 3% O ₂		-
Condition	Location	date	time					
Baseline	run # Run 1	10/26/05	8:43	Cl ₂ < 0.07	HCI 1.91	Br ₂ < 0.01	HBr 0.04	Comments
Baseline	Run 2	10/26/05	9:58	< 0.07 < 0.08	1.61	< 0.01 < 0.01	0.04	
Baseline	Run 3	10/26/05	14:14	0.09	1.28	< 0.01	0.03	chlorine data qualitative, not quantitative
Baseline	Run 4	10/26/05	15:17	< 0.06	1.32	< 0.01	0.03	
CaCl2 injection rate 1 (60ppm i	Run 1	10/27/05	13:37	< 0.08	53.36	na	na	
CaCl2 injection rate 1 (60ppm i		10/27/05	14:41	< 0.08	58.12	na	na	
CaCl2 injection rate 1	Run 3	10/27/05	15:47	< 0.08	48.72	na	na	lost ~2ml of impinger #1 during recovery
CaCl2 injection rate 2 (400ppm		10/28/05	10:56	< 0.08	34.51	na	na	variac off most of the run
CaCl2 injection rate 2 (400ppm		10/28/05	12:04	< 0.08	36.19	na	na	
CaCl2 injection rate 3 (800ppm		10/28/05	14:39	< 0.09	66.94	na	na	
CaCl2 injection rate 3 (800ppm CaBr2 injection rate 1 (4 ppm E		10/28/05 10/29/05	15:41 11:31	0.10 na	67.79 7.35	na < 0.01	na 2.17	chlorine data qualitative, not quantitative
CaBr2 injection rate 1 (4 ppm E		10/29/05	13:20	na	6.44	< 0.01	2.68	
CaBr2 injection rate 2 (8 ppm E		10/29/06	15:18	na	6.62	< 0.01	5.18	
CaBr2 injection rate 2 (8 ppm E		10/29/05	16:21	na	6.37	< 0.01	5.08	
CaBr2 injection rate 3 (0.5 ppm		10/30/05	12:35	na	1.16	< 0.01	0.32	leak in the sample heated line during run
CaBr2 injection rate 3 (0.5 ppm		10/30/05	14:10	na	2.20	< 0.01	0.68	
CaBr2 injection rate 4 (2 ppm E		10/30/05	16:55	na	2.65	< 0.02	2.02	sample line valve off during part of run
Baseline	Run 5	11/2/05	13:44	< 0.05	1.28	< 0.01	0.04	
Baseline	Run 6	11/2/05	15:20	< 0.06	1.42	< 0.01	0.05	missing impinger weight (LISO incorrect)
LT CaBr2 Inject - 2 ppm LT CaBr2 Inject - 2 ppm	Run 1 Run 1	11/5/05 11/6/05	0:00 7:55	na na	2.05 1.57	< 0.01 < 0.01	1.86 1.93	missing impinger weight (H2O incorrect)
LT CaBr2 Inject - 2 ppm	Run 2	11/6/05	9:37	na	1.76	< 0.01	2.18	
LT CaBr2 Inject - 2 ppm with do		11/7/05	7:36	na	1.39	< 0.01	1.99	
LT CaBr2 Inject - 2 ppm	Run 2	11/7/05	9:47	na	1.57	< 0.01	1.98	IGS valve pulled air for ~1 min
LT CaBr2 Inject	Run 1	11/8/05	8:20	na	1.61	< 0.00	1.61	
LT CaBr2 Inject	Run 2	11/8/05	10:44	na	na	na	na	run bad, lab received no sample
LT CaBr2 Inject	Run 1	11/9/05	7:38	na	1.67	< 0.01	1.65	
LT CaBr2 Inject	Run 2	11/9/05	10:01	na	1.64	< 0.01	1.98	
CaBr2	Run 1	11/10/05	7:50	na	2.91	< 0.01	1.79	
CaBr2 CaBr2	Run 2 Run 1	11/10/05 11/11/05	9:36 7:53	na	3.16 4.40	< 0.01 < 0.01	2.00 1.93	
CaBr2	Run 2	11/11/05	9:39	na na	4.40	< 0.01	1.93	
CaBr2	Run 1	11/11/05	8:01	na	1.41	< 0.01	1.46	
CaBr2	Run 2	11/12/05	10:30	na	1.54	< 0.01	1.84	
CaBr2	Run 1	11/13/05	8:56	na	2.83	< 0.01	2.47	missing impinger weight (H2O incorrect)
CaBr2	Run 2	11/13/05	10:46	na	2.89	0.02	1.52	
CaBr2 injection	Run 1	11/14/05	7:54	na	2.17	0.02	1.76	
CaBr2 injection	Run 2	11/14/05	9:45	na	2.62	< 0.01	1.77	
CaBr2 injection	Run 1	11/15/05	8:33	na	1.39	< 0.01	1.67	
CaBr2 injection LT CaBr2 Inject	Run 2 Run 1	11/15/05 11/16/05	10:23 10:35	na na	1.24 1.54	< 0.01 < 0.01	1.48 1.55	missing impinger weight (H2O incorrect) port next to probe open during part of run
LT CaBr2 Inject	Run 2	11/16/05	15:30	na	1.19	< 0.01	1.43	42 low O2 reading during run - leak?
LT CaBr2 Inject	Run 1	11/18/05	9:25	na	3.20	< 0.01	2.00	42 10W 02 roading during run loak.
LT CaBr2 Inject	Run 2	11/18/05	14:05	na	1.77	< 0.01	1.60	
Baseline	Run 1	11/29/05	8:46	< 0.05	4.67	< 0.01	0.09	
Baseline	Run 2	11/29/05	10:36	< 0.05	4.90	< 0.01	0.09	
Baseline	Run 1	11/30/05	7:52	< 0.05	1.89	< 0.01	0.06	
Baseline	Run 2	11/30/05	9:43	< 0.05	1.87	< 0.01	0.06	
Baseline	Run 1	12/1/05	7:56	< 0.04 < 0.04	4.61	< 0.01	0.06	
Baseline CaBr2 Injection	Run 2 Run 1	12/1/05 12/3/05	9:45 9:11	< 0.04 na	5.60 3.83	< 0.01 < 0.02	2.33	clogged IGS filter, run stopped and restarted
CaBr2 Injection	Run 2	12/3/05	10:49	na	0.28	< 0.02	2.33	clogged IGS lilter, furt stopped and restarted
CaBr2 Injection	Run 1	12/4/05	8:12	na	2.87	< 0.02	2.63	
CaBr2 Injection	Run 2	12/4/05	14:07	na	2.85	< 0.02	2.40	
CaBr2 Injection	Run 1	12/5/05	11:15	na	3.33	< 0.01	2.33	
CaBr2 Injection	Run 1	12/6/05	7:54	na	2.48	< 0.01	3.01	
CaBr2 Injection	Run 2	12/6/05	8:54	na	3.23	< 0.02	3.81	
High CaBr2 Inject	Run 1	12/7/05	7:35	na	2.34	< 0.01	3.09	
High CaBr2 Inject	Run 2	12/7/05	8:33	na	2.38	< 0.01	3.00	
High CaBr2 Inject	Run 1	12/8/05	8:18	na	2.39	< 0.02	3.22	
High CaBr2 Inject	Run 2	12/8/05	9:30	na	2.01	< 0.02	4.63	
High CaBr2 Inject High CaBr2 Inject	Run 1 Run 1	12/9/05 12/10/05	8:26 8:13	na	1.79 1.91	< 0.02 < 0.02	3.75 3.63	small leak during run
High CaBr2 Inject	Run 2	12/10/05	10:37	na na	2.32	< 0.02 < 0.02	4.34	Sman reak during furi
High CaBr2 Inject	Run 1	12/11/05	8:02	na	1.57	< 0.02	3.94	
High CaBr2 Inject	Run 2	12/11/05	8:57	na	1.67	< 0.02	4.09	
High CaBr2 Inject	Run 1	12/12/05	8:18	na	1.39	< 0.01	2.80	
High CaBr2 Inject	Run 1	12/13/05	9:58	na	1.07	< 0.01	5.60	
High CaBr2 Inject	Run 2	12/13/05	15:04	na	0.68	< 0.02	0.12	

Mercury Control Technology Phase II Field Testing "Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD"



Project Summary
DE-FC26-O3NT41991

Last Updated: March 31, 2006

National Energy Technology Laboratory





Project Objectives

- Determine the impact of chemical addition on mercury speciation and overall mercury removal from flue gas using the combination of an electrostatic precipitator and a wet scrubber.
- Test the mercury removal technology for a full-scale North Dakota lignite-fired unit at Minnkota Power's Milton R. Young Unit 2.
- Test the mercury removal technology for a full-scale Texas lignitefired unit at TXU's Monticello Unit 3.
- Measure baseline mercury speciation and removal.
- Measure mercury speciation and removal with the control technology.
- Evaluate variability of mercury removal and emissions while applying the control technology.
- Determine the balance-of-plant effects as a result of using the control technology.
- Perform a preliminary economic evaluation.

Partnership Team









North Dakota Industrial Commission































Project Principals

- Project Manager: Steven Benson, Energy & Environmental Research Center (EERC), sbenson@undeerc.org, (701) 777-5177
- Denny McDonald, Babcock & Wilcox
- Stu Libby, Minnkota Power Cooperative
- Bob Weimuth, TXU Energy
- Ramsay Chang, EPRI
- Carl Richardson, URS Corporation
- Project Manager: Andrew O'Palko, U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL)



Budget

Start Date	End Date	Government Cost	Performer Cost	Total Cost	Cost Share
9/26/03	9/25/06	\$1,602,195 Proposed	\$536,335 Proposed	\$2,138,530 Proposed	25%
9/26/03	12/31/05	\$1,602,195 Obligated	\$340,680 Obligated	\$1,942,875 Obligated	Obligated

• DOE Costs to Date: \$1,158,606.42

• Cost Share to Date: \$170,847.82



Highlights of Progress to Date

- Contract negotiated with DOE.
- Site visit by the EERC and Babcock & Wilcox to MRY, December 11, 2003.
- Site visit by URS to Monticello, February 2004.
- Completed hardware design, procurement, and fabrication of hardware common to MRY, Leland Olds, and Antelope Valley Stations under program DE-FC26-03NT41991.
- Installed corrosion probes for baseline testing at MRY and will be removed in early January 2005.
- Completed test plan for MRY.
- Installed SEA skid, PAC injection system, and sampling ports at MRY.
- Removed baseline corrosion probes and replaced them with probes to be exposed during the 4-week test period at MRY.



Highlights of Progress to Date (Cont.)

- Mercury sampling and measuring equipment was brought on-site and installed at MRY.
- Two trailers for on-site analysis, coordination of sampling activities, and preparation of sampling trains were brought on-site at MRY.
- Completed baseline and parametric testing at MRY.
- Completed longer-term testing of SEA and SEA with PAC at MRY.
- Met with URS to discuss results of MRY and possible implications related to application of oxidation technologies to Monticello.
- Completed testing of oxidation technologies for Hg control at MRY and attained about 55% removal
- Sight visits and testing initiated at Monticello.
- Completed testing at Monticello.



Project Tasks and Status

Task	Description	Status
1	Pretest activities, MRY Station	Site visit completed 12/11/04
2	Testing, MRY	Parametric testing completed March 31, 2005; long-term testing completed May 19, 2005.
3	Data reduction and reporting, MRY	In progress
4	Pretest activities, Monticello	Site visit completed 02/04. Draft test plan sent out March 30.
5	Testing, Monticello	Parametric testing occurred on October 27–30, 2005; long-term testing completed December 14, 2005.
6	Data reduction and reporting, Monticello	In progress
7	Final report	Future



Project Milestones

Milestone	Description	Status
1	Negotiate and award contract	Completed
2	Kickoff meeting	Completed
3	Site visit, MRY	Completed
4	Site visit, Monticello	Completed
5	Test plan, MRY	Completed
6	Test plan, Monticello	Completed
7	Quality assurance/quality control (QA/QC) plan, MRY	Completed
8	QA/QC plan, Monticello	Completed
9	Testing, MRY	Completed
10	Testing, Monticello	Completed
11	Site report, MRY	In progress
12	Site report, Monticello	In progress
13	Final report	Future



Project Recognition

- DOE kickoff meeting, November 20–21, 2003
- North Dakota Industrial Commission, November 25, 2003

Newspaper/Print

- "EERC awarded funding for mercury research," Basin Today, Mary Klecker, Magazine Article, Oct/Nov 2003
- "Technology bottleneck slows mercury cleanup: Bush Administration cut power plants slack, but too much?" Washington Post, Guy Gugliotta, March 15, 2004, Newspaper Article
- "Carbon Removal Technique Tops Mercury Tests," Air Daily, Caroline Gentry, Scientific Journal, March 24, 2004
- "Large-scale mercury removal testing begins at LOS," Basin Update, March 31, 2004, Magazine Article
- "EERC lands \$7.9 million in mercury research projects," Associated Press. John McFearson. August 26, 2003.
- "EERC lands over \$7.9 million in contracts for mercury control research," *Newswise*. Associated Press. August 27, 2003.
- "EERC gets \$8 million for research: funds could help state's lignite plants remove mercury emissions before EPA regulations set in," *Grand Forks* Herald. David Dodds. August 28, 2003.
- "UND research center awarded \$7.9 million," Fargo Forum. August 28, 2003.
- "UND research center awarded \$7.9 million," Jamestown Sun. August 28, 2003.
- "\$7.9 million given to help research," Bismarck Tribune. August 28, 2003.
- "DOE approves nearly \$10 million for mercury research at lignite-based plants," *Lignite Update*. September 2003.
- "\$5.8 million funds approved for lignite research," *Larimore Leader*. September 4, 2003.
- "\$5.8 million funds approved for lignite research," *Hatton Free Press.* September 4, 2003.
- "\$5.8 million funds approved for lignite research," Pembina New Era. September 4, 2003.
- "Delegation announces \$5.8 million for UND energy projects," *Medora, Billings County Pioneer.* September 4, 2003.
- "Delegation announces \$5.8 million for UND energy projects," Beach, Golden Valley News. September 4, 2003.
- "EERC lands contract to deal with mercury in coal," Dakota Student. Daryl Sager. September 8, 2003.



Project Recognition (Cont.)

News Releases

- "EERC lands \$7.9 million in contracts for mercury control research," Press Release. EERC.
 Derek Walters. August 26, 2003.
- "Delegation announces \$5.8 million for UND energy projects: Lignite-fired energy plants to take part in research," Press Release. U.S. Senator Earl Pomeroy. August 26, 2003.
- "Conrad announces \$5.8 million for UND energy projects: Lignite-fired energy plants to take part in research," Press Release. U.S. Senator Kent Conrad. August 26, 2003.
- "EERC researchers to receive distinguished service award," Press Release. EERC. Bethany Dennie. November 5, 2003.

TV/Radio Coverage

- "EERC lands \$7.9 million in mercury research projects," 1590 KCNN. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," ND Public Radio. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," KVLY-TV 11. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," WDAZ-TV. August 27, 2003.
- "EERC Mercury Projects." KXJB-TV CBS4, James Degelder. August 28, 2003.
- "EERC Mercury Projects." KVLY-TV 11, James Degelder. August 28, 2003.



Project Deliverables

Deliverable	Description	Status
1	Test plan, MRY	Test Plan completed December 2004
2	Test plan, Monticello	Draft completed March 30, 2005
3	QA/QC plan, MRY	Completed February 2005
4	QA/QC plan, Monticello	Completed
5	Site report, MRY	In progress
6	Site report, Monticello	In progress
7	Final report	In progress



Next Steps and Upcoming Issues

- Upcoming focus areas
 - Complete analysis of samples obtained from the parametric and long-term testing at MRY
 - Characterization of solid samples from MRY testing
 - Complete analysis of data obtained from the parametric and long-term testing at MRY
 - Complete analysis of data obtained from parametric and long-term testing at Monticello
- No current issues of concern

